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VIBRATIONAL SPECTRA and STRUCTURE of POLYATOMIC MOLECULES

being
An Essay in Commemoration of the Fortieth
Anniversary of the National University of
Peking

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TO MY WIFE

KUAN-SHIH YUAN WU

PREFACE

During the last ten years or so, considerable amount of information concerning the structure of polyatomic molecules has been obtained through the theoretical studies with the help of the wave mechanics on the one hand, and the experimental investigations of the infrared and the Raman spectra on the other. Lately, there has appeared a number of books and monographs which taken together cover every aspect of the subject. Schaefer and Matossi's Das Ultrarote Spektrum, Kohlrausch's Der Smekal-Raman Effekt and the recent Ergänzungsband, Sponer's Molekülspektren, Stuart's Molekülstruktur, the chapters by Teller and by Mecke in Eucken-Wolf's Hand-und Jahrbuch der chemischen Physik, Bd 9/II, Plazcek's article in Marx's Handbuch der Radiologie, Bd 6/II, 2nd edition, and Dennison's article in the Review of Modern Physics, Vol. 3, 1931, deal with either the empirical or the theoretical side of the problems of the vibrational spectra of molecules. Some explanation would indeed be necessary for the present attempt to deal with the same subject that has already been so adequately treated.

Just before the present Sino-Japanese war in 1937, the Physics Department of the National University of Peking was planning to start some work in the field of spectroscopy. A course on molecular spectra was organized. The treatment of the theoretical parts of the subject was largely based on the works of Dennison and Teller. In presenting the experimental data and their interpretations, it was felt that the treatments of the individual molecules in the afore-mentioned works are usually by necessity too brief and in a few cases they need some changes in view of more recent experimental data. Since the war, the University was forced to move, first to Chang-sa, and later here. With the complete lack of laboratory equipments, to go on with the projected work becomes impossible. It is thought, however, that opportunity might be taken of the reduced teaching duty and the suspension of experimental work to survey the field in a more detailed and critical manner. The following pages are the result of incorporating some of the more recent investigations into some former notes.

In view of the existence of the above mentioned and other works, it seems best to confine this work to the vibrational spectra of polyatomic molecules and the informations obtainable from them. Even then, no attempt is made at comprehensiveness: rather only those still comparatively simple molecules are treated for which there exist sufficient data. The emphasis has been laid more on the individual molecules than on the systematics of the spectra of molecules containing similar structural groups. For the latter, reference should be made to Kohlrauch's Ergänzungsband (which is unfortunately not available to the writer). The studies, in the last few years, of molecular association by means of the spectra have not been reviewed in detail; for while it is easy to understand in a qualitative manner the frequency shifts arising from the formation of hydrogen bonds, both quantitative measurements and a quantitative theory do not seem to be at hand. Also the calculations of thermodynamic functions from spectroscopic data have only been briefly summarized, for except in two or three cases (ethane, benzene) these functions are more of chemical than physical interest. An elementary exposition and summary are given of the theoretical background on which the discussions of the empirical data are based, in the hope that they may serve as an introduction to the subject for those not already familiar with the work in this field. A little knowledge of the wave mechanics is assumed. In the main, these introductory chapters are based on the above-mentioned works, in particular, of Dennison and of Teller, to which frequent references are made.

On account of the lack of adequate library facilities, it has not been found possible, nor indeed useful, to quote all the original papers on the subject. For this the writer may perhaps be pardoned, since the works of Schaefer and Matossi, Kohlrausch, Stuart and Sponer give adequate references to practically all earlier papers. It will be obvious that the discussions of the different molecules in Chap. V are far from being uniform. This is necessary from the nature of the molecules and of the data that are available. More weight has naturally been given the high dispersion infrared investigations of which the Michigen Laboratory has perhaps made the most signal contributions. It will be noted how much more definite informations can be derived from a high dispersion and high resolution study than from a low dispersion work which merely locates the positions of the bands. Let us hope that in the near future, many of the molecules for which only tentative discussions are given here will be subjected to high dispersion investigations.

The writer is indebted to the many authors from whose works he has drawn so freely, and in particular to Professor D. M. Dennison from whom he first learned the subject of molecular spectra. To the University, he is grateful for arranging to publish this work on the occasion of its Fortieth Aniversary. Finally, he wishes to express his gratitude to his teacher and friend, Professor Y. T. Yao, Director of the Physics Laboratory, but for whose inspiration this work would not have been attempted.

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June, 1939.

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CHAPTER I

INTRODUCTION: METHODS OF STUDYING MOLECULAR STRUCTURE

A molecule may be conceived as a number of atomic nuclei imbedded in the field of a distribution of electrons, or as a number of electrons in the field of the nuclei. Just as in an atom, the electrons in a molecule are capable of existing in different energy states. This is established in a direct manner, besides by the results of the analyses of the spectra of molecules, by experiments on the excitation of molecules by electron impacts—similar to the Franck-Hertz experiment for the atoms. In a given electronic state, there is an equilibrium configuration for the atomic nuclei. Now the questions that first present themselves are the following: What are the geometrical form and the dimensions of a molecule in a given electronic state, and in particular, in the normal state? What is the distribution of the electrons? What is the nature of the binding of the different atoms in the molecule? We shall see that informations concerning these different aspects of the problem of molecular structure can be obtained from a variety of experimental and theoretical studies. We shall mention briefly a few of the more direct and fruitful methods in this chapter and devote the rest of the present volume to the discussion of the methods and results obtained from the study of the vibrational spectra of polyatomic molecules.

§1. Non-spectroscopic Methods

A) Permanent Electric moment Measurements

From measurements of the permanent dipole moment of a molecule, one learns about the distribution of the electric charges in the molecule. Thus a zero moment indicates in general a symmetrical distribution. From the dipole moments of a series of molecules containing a certain chemical bond or a certain radical, it is possible to deduce a value for the dipole moment of the bond or radical, the assumptions being made that there is a definite meaning in ascribing a moment to a bond or radical, and that in a molecule these bond and group moments add together vectorially without greatly affecting the value of one another. This method is useful in deciding between two or more possible structures for certain molecules. It is subject, however, to the following limitations: On the one hand, the above assumption that the moments of different bonds or groups simply add vectorially in a complex molecule is not always valid on account of the induction effect. On the experimental side, it is not always practicable to measure the dipole moments of molecules in the gaseous state, and measurements in the liquid state and in solutions are subject to a number of disturbing factors for which corrections have to be made, sometimes only with difficulties and in a semi-empirical manner.

B) Polarization of Scattered Radiations and Kerr Effect

Information concerning the symmetry properties of the electric charge distribution in a molecule can also be obtained through a study of the polarization characters of the coherent scattered radiations (Rayleigh scattering) from the molecule. The scattering process is determined by the polarizability of the molecule, which is in general an ellipsoid. For a molecule which is spherically or tetrahedrally symmetric, the ellipsoid becomes a sphere and an electric moment can be induced with equal ease in all directions. The scattered radiation will in this case be polarized (that is, the electric intensity of the scattered radiations lies in the same direction as that in the incident radiations). In a molecule in general, however, because of the anisotropy, the induced electric moment will not correspond exactly to the direction of the electric vector of the incident radiations and the scattered radiations will be partially depolarized, the degree of depolarization being determined by the structure of the molecule. Thus measurements of the depolarization of the scattered radiations will throw light on the problem of the symmetry of the molecule.

The appearance of double refraction in a substance when placed in an electric field is also closely related to the polarizability of the molecule. A partial orientation of the molecules as the result of the induced moment in the field brings about a difference in the behavior of the molecules in different directions under the action of the incident radiations. From measurements of the so-called Kerr constant of a molecule, it is possible to derive certain information concerning the anisotropy of the polarizability tensor of the molecule.

C) X-ray and Electron Diffraction Measurements

When a monochromatic beam of X-ray or electrons of suitable energies is directed through a gas or vapor and the diffracted beam received on a photographic plate perpendicular to the original beam, certain intensity patterns are obtained which are symmetrical about the geometrical center of the beam and are characteristic of the particular molecule under investigation. The theory of Debye enables a correlation to be made between the intensity pattern and the internuclear distances in the molecule. By comparing the observed pattern with the theoretical pattern calculated with various assumed internuclear distances, it is possible to determine these distances. These methods have been extensively used in recent years and have yielded the most direct values for the internuclear distances of molecules. They are, however, subject to the following limitations: As the diffraction of X-rays is mainly determined by the electrons in the molecule, the accuracy of the determination of the internuclear distances depends on the accuracy with which the electron distribution is known, or, since this distribution is usually not known with high accuracy, on how good the approximate distribution is. The diffraction of electrons of 40000-50000 volts energies is, however, mainly a nuclear process and the calculated intensity pattern is mainly determined by the nuclear distances. In this case, only the relatively heavy atoms in a molecule contribute appreciably to the diffracted intensity pattern, and to molecules composed of light atoms such as H and D, this method cannot be applied. In this respect, this method and the method of infrared spectroscopy are complementary.

§2. Molecular Spectra

Just as in an atom the electrons in a molecule can exist in different energy states. The energy differences between these states can be expected to be in general of the same order as in the atoms. Hence a transition from one to another of these states, when accompanied by a change in the electric moment of the system, will give rise to the emission or absorption of radiation whose frequency is determined by the relation

$$h\nu = (E_{el})_m - (E_{el})_n \tag{1}$$

and lies usually in the visible or the ultraviolet region of the spectrum.

In any electronic state, there must be an equilibrium configuration for the atomic nuclei for the molecule to be stable at all. One may thus consider the molecule as a system of particles in stable equilibrium in a potential field. Such a system can, according to mechanics, execute vibrations about the position of equilibrium. The frequencies of these vibrations are determined by the masses of the atoms and by the potential field.(1) They lie approximately between ca. 3500 cm^{-1} (ca. 3μ) in molecules containing the lightest atom H, and 300 cm^{-1} ($\sim 30\mu$) or even lower in molecules containing such heavy atoms as Br or I. According to the quantum theory, the vibrational energy of a molecule is quantized so that there are discrete states with different energies. If in a transition from a vibrational state v to a higher state v′ there is a change in the dipole moment of the system (electrons and nuclei), radiation of frequency given by

$$h\nu_v = (E_{vib})_{v'} - (E_{vib})_v \tag{2}$$

will be absorbed. From a study of the near infrared spectrum ($1\text{-}30\mu$), informations concerning the vibrational states of the molecules can be obtained.

In addition to the electronic motion and the vibrations of the atoms, a molecule can rotate as a whole. According to the quantum theory, the rotational energy of a molecule is also quantized so that there are discrete states with different energies. The frequency associated with a change of the rotational state

$$h\nu_r = (E_{rot})_{r'} - (E_{rot})_r \tag{3}$$

is in general of the order 20-200 cm^{-1} depending on the moments of inertia of the molecule. Transitions between the rotational states, if the molecule possesses a permanent electric moment, will give rise to the emission or absorption of radiation in the far infrared spectrum ($50\text{-}500\mu$). This spectrum is called the pure rotational spectrum.

When there is a simultaneous change in the vibrational and the rotational states of a molecule, the frequency of the radiation will be given, in a first approximation, by adding (1) and (2),

$$h\nu = (E_{vib} + E_{rot})_{v'r'} - (E_{vib} + E_{rot})_{vr} = h(\nu_v + \nu_r) \tag{4}$$

Since $\nu_v \gg \nu_r$, the general position of the radiation in the spectrum will be that of ν_v; but now the radiation, instead of the single frequency (2), has a large number of frequencies corresponding to different changes in the rotational states. The spectrum is then a large number of lines forming a band, which is called a vibration-rotational band.

When there is a simultaneous change in the electronic, vibrational and rotational states of a molecule, the frequency of the radiation is given in a first approximation by adding (1) and (4), which lies in the general region determined by (1) since $E_{el} \gg E_{vib}$. Various transitions in (4) for a given transition (1) form a system of electronic bands. From the analyses of such bands, informations concerning the excited electronic state as well as the normal state can be obtained. Unfortunately, comparatively few polyatomic molecules thus far studied show discrete electronic bands, although valuable informations can also be obtained from the continuous absorption spectra. In the present volume, we shall not be concerned with these electronic transitions, but shall rather confine ourselves to the considerations of polyatomic molecules in their normal electronic state, *i.e.*, to the study of the vibration-rotational spectra of polyatomic molecules.

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(1) Since the vibrational motions are relatively slow compared with the motions of the electrons on account of the great difference in their masses, the electronic structure will be able to adjust itself during these vibrations. It is with a sort of averaged potential field during these vibrations that we are dealing.

While the positions of the vibration-rotational bands of a molecule are determined by the masses of the atoms and by the potential field, the structure of the bands is determined by the following factors: (1) the symmetry properties of the molecule, (2) the directions of the change of the electric moment due to the vibration, relative to the elements of symmetry of the molecule, and (3) the values of the principal moments of inertia of the molecule. Also by taking into consideration the interaction between the vibration and the rotation of the molecule in (4), certain features in the band structure can be explained. Hence with the help of the theory, the study of the positions and the detailed structure of the bands will furnish one with the following informations concerning: (1) the symmetry properties of the molecule, (2) the nature of the potential field, *i.e.*, the nature of the binding of the atoms in the molecule, and (3) the moments of inertia and consequently the dimensions of the molecule. In some cases, such informations cannot be obtained by other means and the study of the vibrational spectra becomes then indispensable.

The vibrational spectrum of a molecule can be studied in absorption and in scattering (Raman effect). Experimentally, the study of the infrared spectrum requires a technique completely different from that for the visible or the ultraviolet region. Briefly, the experiment consists in passing the radiation from a suitable continuous source (usually a Nernst glower for the near infrared, and a gas mantle for the far infrared) through the substance under investigation (preferably in the gaseous state, but may also be liquids, crystals or solutions).The radiation is focussed, by means of mirrors so as to avoid chromatic aberrations, on the slits of a spectrometer. This may be a prism instrument (fluorite prism may be used up to $\sim 7\mu$, rocksalt to $\sim 15\mu$, KBr to 26μ, KI to

$\sim 30\mu$) if the required dispersion is not great. A grating of the echelette type with the proper ruling space must be used for high dispersion and resolving power. To avoid the overlapping of different spectral orders in the grating instrument, a prism-grating combination has been devised in which a narrow energy band in the desired spectral region is obtained and isolated by means of a fore prism of the suitable material and this narrow energy band is further analyzed by a grating. In the far infrared where the prism technique is not applicable, the purification of the spectral energy is often achieved by means of filters and by reflections from Reststrahlen crystals or pressed plates. In the case of a prism instrument, wave length measurements can be made either from the positions of minimum deviation of the prism and the known dispersion curve of the prism material, or by means of an empirical calibration curve obtained with infrared atomic lines and molecular bands whose wave lengths are known. With the grating instrument, the wave lengths may be obtained from the positions and the constants of the grating.

Perhaps the greatest experimental difficulty in infrared investigations is the detection of the radiation, which is now usually done by means of sensitive thermocouples. To increase the sensitivity, the thermocouples are housed in high vacuum. This necessitates a housing with a suitable material for the window to permit the entry of the radiation to be measured. To reduce the "drift" of the galvanometer due to changes in the temperature of the surrounding, one may employ two junctions in opposition, with one of them exposed to the radiation to be measured. The small current generated in the thermocouple may be amplified by certain devices and measured by a sensitive galvanometer. The amplification is limited, however, by the unsteadiness of the system on account of the Brownian motions.

Theoretically, it would be desirable to employ as high a dispersion and resolution as possible so as to obtain the structure of a band down to the greatest details. This is limited, however, by the practical difficulty of measuring too small an amount of energy in the infrared. This is a disadvantage compared with the technique in the photographic region in which the integrating effect may be used. Now one meets with no great difficulty in obtaining a resolution of lines as close as 0.5 cm^{-1} throughout the whole region 1-100μ, although a great deal of the work in this field has been done with a much smaller resolution. This is due to the fact that the amount of manual work required to cover a given spectral region increases very much as one increases the dispersion and the resolving power of the instrument.

On the experimental side, certain spectral regions, for example 30-40μ, present some difficulties in that there is no satisfactory material for the window of the thermocouple, and a high sensitivity of the detecting device is essential in work of high resolution. For this reason, the spectra of molecules composed of relatively heavy atoms remain mostly unexplored in this region. On the other hand, the method of electron diffraction is best adapted to such molecules. Also the data from the Raman effect are most useful for these low frequencies.

The Raman spectrum of a molecule excited by a monochromatic radiation consists, as is well known, of a number of lines whose frequency differences with that of the exciting radiation are equal to the vibrational frequencies of the molecule. Thus certain low frequencies which lie in a region not easily accessible by the infrared technique can be obtained from the Raman spectrum. Also in molecules possessing certain elements of symmetry, not all the normal vibrations will appear in the absorption spectra. In such cases, the selection rules are usually such that vibrations that appear in the infrared do not appear in the Raman spectrum, while those appearing in the Raman spectrum do not appear in the infrared. Thus the combined data of the infrared absorption and the Raman spectra are necessary for obtaining the vibrational frequencies of the molecule.

In the following three chapters, we shall present the theory of the vibrational spectra of polyatomic molecules on which the interpretations of the observed infrared and Raman data are based. In Chapter V, we summarize the results that have been obtained for a number of molecules. It is beyond the scope of this work to attempt a discussion of the experimental technique, the theory of electronic structure of polyatomic molecules, and the theory and results of the non-spectroscopic methods mentioned in §1 of this chapter. The following list of general references will perhaps be helpful for the reader who wishes to go into these subjects.

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(2) H. A. Stuart, *Molekülstruktur,* 1934, (Kerr effect and dipole moments)

(3) P. Debye & H. Sack, Chapter in Marx's *Handbuch der Radiologie,* Bd VI/2, 2nd. Ed. 1934, (theory and results on the electrical properties of molecules)

(4) P. Debye, *Dipole Moments and Chemical Structure* (Leipziger Vorträge, 1929)

(VII) Electron Diffraction measurements

(1) L. O. Brockway, Review of Modern Physics, 8, 231 (1936)

(2) Brockway and Taylor, Chapter in Annual Reports, Chemical Society, London, 1937

(3) S. Glasstone, Annual Reports, Chemical Society, London, 1936

(VIII) Electronic Structure and Chemical Valence

(1) G. W. Penney, *The Quantum Theory of Valence,* Methuen, 1935

(2) J. H. Van Vleck and A. Sherman, Review of Modern Physics, 7, 167, (1935)

(3) W. Heitler, Chapter in Marx's *Handbuch der Radiologie,* Bd VI/2, 2nd Ed. 1934

CHAPTER II

VIBRATIONS OF MOLECULES: CLASSICAL THEORY

§1. Normal Vibrations and Normal Frequencies

The problem of the vibrations of the atoms in a molecule from their positions of equilibrium can be treated by the well known methods of classical mechanics. An infinitesimal displacement of the atoms from their equilibrium positions brings about restoring forces depending on their relative displacements. The equations of motion of the atoms can be solved if the forces are known functions of the relative coordinates of the atoms. When the amplitudes of motion of the atoms are very small compared with the normal interatomic distances, the solution of the equations of motion is particularly simple, as we shall see below.[1]

A molecule composed of N atoms possesses $3N$ degrees of freedom, of which three are the translational motion of the molecule as a whole, and for non-linear molecules three are the rotational motion of the molecule. There are thus $3N-6$ degrees of freedom for the vibrations of the atoms in the molecule, for the description of which one needs $3N-6$ coordinates. Let us denote the generalized coordinates specifying the relative positions of the atoms by Q_1, $Q_2, \ldots . Q_n$ where $n=3N-6$, and let the values of these coordinates in the equilibrium configuration be Q_1°, $Q_2^\circ, \ldots . Q_n^\circ$ so that

$$Q_i = Q_i^\circ + q_i, \qquad i = 1, 2, \cdots\cdots n. \tag{1}$$

The q's are then the relative displacements from the equilibrium configuration. The kinetic energy of the vibrational motion of the system of atoms is in general of the form

$$T = \tfrac{1}{2} \sum_{i,j} a_{ij} \dot{q}_i \dot{q}_j \tag{2}$$

where the a_{ij}'s are functions of the masses of the atoms and the coordinates Q_i's. The potential energy of the system, on the assumption of infinitesmal displacements q's, can be expanded in a series in terms of the q's,

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[1] For a treatment of the normal vibrations, see for example Webster, *The Dynamics of Particles, and of Rigid, Elastic & Fluid Bodies;* also Whittaker. *Analytical Dynamics.*

$$V(Q_1, Q_2 \cdots\cdots Q_n) = V(Q_1^\circ, Q_2^\circ \cdots Q_n^\circ) + \sum_i \left(\frac{\partial V}{\partial Q_i}\right)_\circ q_i$$
$$+ \tfrac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V}{\partial Q_i \partial Q_j}\right)_\circ q_i q_j + \cdots\cdot. \tag{3}$$

Since by hypothesis the configuration represented by Q_1° , Q_2° , ... Q_n° is one of equilibrium, all the generalized force components vanish at Q_1° , Q_2° , . . . Q_n° . On neglecting terms in (3) which are small quantities of order higher than the second, and on denoting $\left(\frac{\partial^2 V}{\partial Q_i \partial Q_j}\right)_\circ$ by b_{ij}, one has

$$V - V^\circ = \tfrac{1}{2}\sum_{i,j} b_{ij}\, q_i\, q_j \tag{4}$$

for the potential energy relative to the equilibrium configuration.

The coefficients a_{ij} in the kinetic energy expression (2) can, on the assumption of small displacements q's, be expanded about the equilibrium configuration

$$a_{ij}(Q_1, Q_2 \cdots Q_n) = a_{ij}(Q_1^\circ, Q_2^\circ, \cdots Q_n^\circ) + \sum_k \left(\frac{\partial a_{ij}}{\partial Q_k}\right)_\circ q_k + \tfrac{1}{2}\sum_{k,l}\left(\frac{\partial^2 a_{ij}}{\partial Q_k \partial Q_l}\right) q_k\, q.$$

Substituting into (2) and neglecting small quantities of order higher than the second, one obtains

$$T = \tfrac{1}{2}\sum_{i,j} a_{ij}^\circ\, \dot{q}_i\, \dot{q}_j. \tag{5}$$

By its nature, the kinetic energy T must be a positive definite quadratic form, and since the equilibrium configuration must be a stable one for the molecule to be stable at all, the potential energy $V - V^\circ$ must also be a positive definite quadratic form. A theorem in algebra enables one to find one, and only one, linear transformation

$$q_i = \sum_j c_{ij} X_j \tag{6}$$

such that by it the two quadratic forms for T and $V - V^\circ$ are brought simultaneously into the normal forms

$$2T = \sum_i \dot{X}_i^2, \qquad 2V = \sum_i \lambda_i X_i^2, \tag{7}$$

where V has been written for $V - V^\circ$. The λ's are the roots of the determinantal equation

$$\begin{vmatrix} a_{11}\lambda - b_{11} & a_{12}\lambda - b_{12} \cdots & a_{1n}\lambda - b_{1n} \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ a_{n1}\lambda - b_{n1} & a_{n2}\lambda - b_{n2} \cdots & a_{nn}\lambda - b_{nn} \end{vmatrix} = 0 \tag{8}$$

The coefficients c_{ij}'s in the transformation equations (6) are proportional to the values of the minors of the elements $a_{ij}\lambda - b_{ij}$ in the determinant (8) when λ is given the value of the jth root, *i.e.*, $\lambda = \lambda_j$.

Application of the Lagrange equations to (7) gives n equations of the form

$$\ddot{X}_i + \lambda_i X_i = 0, \qquad i = 1, 2, \cdots n, \tag{9}$$

which are the familiar equations of simple harmonic motions. Solution of (9) gives

$$X_i = A_i \cos(2\pi\nu_i t - \varepsilon_i), \tag{10}$$

$$\nu_i = \frac{1}{2\pi}\sqrt{\lambda_i} \qquad i = 1, 2, \cdots\cdots n.$$

As the λ's are the roots of (8), their values depend on the coefficients a_{ij} and b_{ij} in the kinetic and the potential energy expressions. They may be all distinct, but there may also be double or triple roots. Thus in general, in a molecule consisting of N atoms, there are $3N-6$ fundamental frequencies, not all of which need be distinct but there may be double or triple frequencies. When a number of vibrations has the same frequency, the vibrations are said to be degenerate. We shall see later that the presence of degenerate vibrations is conditioned by the symmetry of the molecule alone, but is in general independent of the numerical values of the coefficients a_{ij} and b_{ij} except for the case of accidental degeneracy (Chap. III, §4, B).

Equations (6) show that in general during the vibrational motion of a molecule, each coordinate q is a linear combination of n simple harmonic vibrations X's; and from the inverse transformation of (6), namely,

$$X_i = \sum_j d_{ij}\, q_j, \tag{11}$$

it is seen that each normal vibration X involves the motion of all the atoms of the molecule. (In some cases certain coefficients c_{ij} and d_{ij} vanish as the result of some symmetry properties of the molecule and its vibrations. See (28) and also Chap. V, (47).)

From equations (8), it follows that an *a priori* knowledge of the potential function would enable one to determine the frequencies of the normal vibrations. Conversely, from the experimentally observed frequencies, one can calculate a number of constants in the potential function equal to the number of distinct frequencies of the molecule. When the number of unknown potential constants is less than the number of distinct frequencies, the extra relations from (8) may serve as a test for the consistency of the calculation; while if the reverse is the case, an unique determination of the potential function is usually impossible. In such cases, recourse must be made to other methods such as the isotope effect (§7) and theoretical or empirical knowledge concerning the potential function of the molecule. These will be discussed in Chap. V when dealing with the actual molecules.

The above classical theory will not only enable one to determine the potential function from the frequencies or *vice versa*, but also give, through the transformation equations (6), the relative sense and magnitude of the displacements of the individual atoms in each normal vibration, and hence the relative amounts of energy associated with each atom or group of atoms. In many cases a knowledge of the forms of vibrations corresponding to the observed frequencies is important for a clear understanding of the potential function of the molecule. We shall have occasion to discuss such cases in Chap. V.

Finally, let us consider briefly the question concerning the choice of the coordinates in (1) for a given molecule.[2] The coordinates Q's which are $3N-6$ in number are called the "internal" coordinates since in terms of them the translational and the rotational parts of the kinetic energy are separated from that of the vibrational motions. For a molecule possessing certain elements of symmetry, a particular choice of these coordinates can be made so that the determinantal equation (8) can be immediately factored, thus reducing the labor of the solution. The disadvantage with the use of these internal coordinates is the difficulty of obtaining the kinetic energy (2) in terms of them except in the case of very simple systems.

Another alternative choice of coordinates is the $3N$ rectangular coordinates themselves. In terms of them, the kinetic energy can be immediately written down; but then the potential energy (let us say, of the valence force type, see §3) will in general take on a complicated form and the determinantal equation will contain 6 more rows and columns and 6 zero roots. A particular case of these "external" coordinates is the "external symmetry coordinates" which are linear combinations of the rectangular coordinates chosen on considerations of the symmetry of the system in such a way that the determinantal equation (8) can be immediately factored.

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[2] For a discussion of the choice of the coordinates, see E. B. Wilson, Jr. & B. L. Crawford, Jour. Chem. Phys. 6, 223, (1938). External coordinates, O. Redlich & H. Tompa, Jour. Chem. Phys. 5, 529, (1937); Geometrical symmetry coordinates, J. E. Rosenthal & G. M. Murphy, Rev. Mod. Phys. 8, 317, (1936); Symmetry coordinates of E. B. Wilson, Jr., & J. B. Howard, Jour. Chem. Phys. 2, 630, (1934).

Wilson and Howard have employed the "symmetry coordinates" which have the following properties: (*i*) In terms of them, the kinetic energy takes on the form (7), and hence they contain the masses of the atoms in the system, (*ii*) they effect a factorization of the determinantal equation for molecules possessing symmetries. With these coordinates, the determinantal equation can be solved with ease; but the difficulty is shifted to obtaining the correct set of coordinates satisfying the above requirements.

Fortunately, in the case of the molecules with which we are going to deal in Chap. V—molecules for which sufficient data are available for a discussion of the vibrational motions—, the question as to the choice of the coordinates is not a serious one since the molecules are after all still relatively simple systems. In Chap. V, we shall give the normal coordinate treatments for a number of molecular models.

§2. Approximate Method

The results of the last section are exact if the potential energy of a molecule for vibrations can be exactly described by a function which is quadratic in the coordinates. In an actual molecule, however, both theoretical considerations and empirical data show that a quadratic potential can only be regarded as a first approximation to the actual potential. An attempt to employ a more complicated potential than the quadratic function is, however, not practicable not only because of the greater number of unknown constants introduced into the potential function, but also because of the fact that it would no longer be possible to solve the equations of motion in such a simple manner by the use of the normal coordinates. This reduction of the problem of the vibrations of a molecule to that of the normal vibrations is not only desirable in the classical treatment, but is of importance in the quantum theory treatment in that the Schrödinger equation of the system can be separated and solved exactly, thus providing an initial approximation upon which the perturbation method may be based. It will be seen in Chap. V that this method is satisfactory with almost all the molecules that have been studied.

With some molecules in which certain atoms are more strongly bound together than they are with other parts of the molecule, it is sometimes even justifiable to employ the following approximate method: Consider a molecule possessing n degrees of freedom for vibration and hence requiring n coordinates for the specification of the relative positions of the atoms. Suppose one knows already the frequency of vibration when each of the relative coordinates, for example, the relative displacement between a pair of atoms, alone undergoes a simple harmonic vibration, the rest of the molecule being imagined non-existent. Let these n frequencies be ν_1', ν_2',$\cdots\cdots$$\nu'_n$. These n frequencies are then the approximate frequencies of the molecule, and in this approximation the determinantal equation (8) consists simply of the elements $\lambda - \lambda_i'$ along the diagonal, all the non-diagonal elements being zero. These approximate frequencies of course differ from the actual frequencies of the molecule since we have completely neglected the effect of the mechanical coupling (given by the cross terms in the kinetic energy) and the electrical coupling (given by the cross terms in the coordinates in the potential energy) between the various parts of the molecule. To take these into account, we may introduce these as perturbations. The perturbation theory gives for the frequencies of the perturbed system the secular equation[1]

$$\begin{vmatrix} -\lambda + \lambda'_1 & \varepsilon_{12} & \varepsilon_{13} \cdots\cdots \varepsilon_{1n} \\ \varepsilon_{21} & -\lambda + \lambda'_2 & \cdots\cdots \varepsilon_{2n} \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \varepsilon_{n1} & \varepsilon_{n2} & -\lambda + \lambda'_n \end{vmatrix} = 0. \tag{12}$$

It can be shown that, when the perturbing terms are small, the normal frequency ν_i is given by

$$\lambda_i = \lambda'_i + \sum_{j \neq i} \frac{\alpha_{ij}}{\lambda' - {}_i{}'\lambda_j} \lambda_j, \tag{13}$$

where ν'_i is the ith frequency of the uncoupled system. Equation (13) states that each of the original frequencies, say ν'_i, is modified somewhat by the effect of the other vibrations ν'_j, $\nu'_j \neq \nu'_i$, depending on the coefficient α_{ij} which measures the coupling between the vibrations ν'_i and ν'_j. A useful relation among the frequencies ν_i is

$$\Sigma \lambda_i = \Sigma \lambda'_i \tag{14}$$

which follows from (13). A knowledge of the frequencies ν'_i and the coupling coefficients would thus enable one to obtain an approximate estimate of the normal frequencies ν_i. This method is useful in the case of such molecules as composed of well defined chemical bonds or radicals for which the characteristic frequencies can be given the values known from other molecules containing them. Because of the approximate nature of the perturbation method and also because of the uncertainties in the values to be ascribed to the frequencies ν'_i, the results so obtained can be expected to be only approximate and the treatment of the last section is to be preferred wherever it can be carried out.

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[1] See cf. R. Mecke, *Hand-u. Jahrbuch d. Chem. Phys.* 9/II, P. 336; Zeits. f. Physik 103, 291, (1937).

§3. Potential Functions

In a diatomic molecule, the potential energy as a function of the internuclear distance can often be determined over a rather large range of distance from the data on its spectrum, and in a few particularly simple cases the potential energy can even be theortically calculated for a given electronic state of the molecule. In a polyatomic molecule, the complexity of the situation is such that a theoretical calculation of the potential energy is not yet feasible. On the assumption that the potential energy of vibration of a polyatomic molecule may be expanded into a series of terms each of which is a product of the coordinates, it is possible to determine the potential up to terms quadratic in the coordinates from the vibrational spectrum as is shown in §1. In a few cases for which there are sufficient appropriate data, it may even be possible to determine the potential up to terms that are cubic and quartic in the coordinates. In general, however, the quadratic potential already contains more unknown constants than can be determined from the vibrational spectrum. Hence for practical purposes, it is necessary to choose some simpler forms for the potential than would be required by the most general considerations.

The simplification of the potential function must in each case be guided by physical considerations or by empirical knowledge of the structure of the molecule, and is necessarily not unique. The usefulness of a simplified potential must be tested by a comparison with the experimental data in each case. The most useful simplified potential function is the so-called valence force system introduced by Andrew and by Mecke.[1] In some cases the central force system introduced by Dennison[2] is applicable. In still other cases, a potential which is the most general consistent with the symmetry of the molecule may be necessary. The distinction among these various potentials can best be made clear by using a triatomic molecule as an example. Further discussions of these potentials will be given in Chap. V in connection with the individual molecules.

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[1] R. Mecke, Leipziger Vorträger, (1931); Zeits. f. Phys. Chem. B, 16, 409, 421; B 17, 1 (1932); D. H. Andrews, Phys. Rev. 36, 544, (1930).

[2] D. M. Dennison, Astrophys. Jour. 62, 84, (1925); Phil. Mag. 1, 195, (1926).

A) Central Force Treatment

Dennison introduced the central force system according to which each atom in a molecule when displaced from its position of equilibrium is subject to a restoring force which is central about the position of equilibrium. Consequently the potential energy depends only on the magnitudes of the relative displacements of the atoms but is independent of their directions. Thus for a molecule formed by three atoms m_1, m_2, m_3 at distances r_{12}, r_{23}, r_{31} apart, the potential energy for small displacements is, on neglecting the cross terms in the relative displacements,

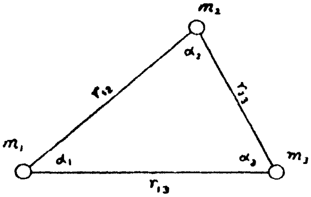

Fig. 1

$$V = \tfrac{1}{2}\left[k_1(\delta r_{12})^2 + k_2(\delta r_{23})^2 + k_3(\delta r_{31})^2\right]. \qquad (15)$$

With this potential, the determinantal equation (8) gives the following relations among the three roots λ's[1]

$$\lambda_1 + \lambda_2 + \lambda_3 = \frac{k_1}{\mu_1} + \frac{k_2}{\mu_2} + \frac{k_3}{\mu_3}$$

$$\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1 = \frac{k_1k_2}{\mu_1\mu_2} + \frac{k_2k_3}{\mu_2\mu_3} + \frac{k_3k_1}{\mu_3\mu_1} - \frac{k_1k_3}{m_1^2}\cos^2\alpha_1 - \frac{k_2k_1}{m_2^2}\cos^2\alpha_2 - \frac{k_3k_2}{m_3^2}\cos^2\alpha_3,$$

$$\lambda_1\lambda_2\lambda_3 = k_1k_2k_3\left[\frac{1}{\mu_1\mu_2\mu_3} - \frac{\cos^2\alpha_1}{\mu_2 m_1^2} - \frac{\cos^2\alpha_2}{\mu_3 m_2^2} - \frac{\cos^2\alpha_3}{\mu_1 m_3^2} + \frac{2\cos\alpha_1\cos\alpha_2\cos\alpha_3}{m_1m_2m_3}\right], \quad (16)$$

$$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_2}, \qquad \frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_3}, \qquad \frac{1}{\mu_3} = \frac{1}{m_3} + \frac{1}{m_1}.$$

For molecules of the type YX_2 represented by an isoceles triangle so that $m_1 = M$, $m_2 = m_3 = m$, $k_1 = k_3 = k$, $k_2 = k'$, $\alpha_1 = \alpha$, equations (16) become

$$\lambda_1 + \lambda_2 = \frac{2k'}{m} + \frac{k}{m}\left[1 + \frac{2m}{M}\cos^2\frac{\alpha}{2}\right],$$

$$\lambda_1\lambda_2 = \frac{2kk'}{m} \cdot \frac{2m + M}{mM} \cdot \cos^2\frac{\alpha}{2},$$

$$\lambda_3 = \frac{k}{m}\left[1 + \frac{2m}{M}\sin^2\frac{\alpha}{2}\right]. \qquad (17)$$

The non-appearance of k', the force constant between the two similar atoms m, in the equation for λ_3 shows that up to this approximation the vibration ν_3 involves no relative displacement between the two m atoms. The forms of the three vibrations are shown in Fig. 2.

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[1] Radakovic, Wien. Ber. 139, 107, (1930).

Two particular cases of the YX_2 molecule are the following:
(i) Linear and symmetrical YX_2

On setting $\alpha = \pi$, equations (17) become

$$\lambda_1 = \frac{2k'}{m} + \frac{k}{m}, \qquad \lambda_2 = 0, \qquad \lambda_3 = \frac{k}{m} \cdot \frac{2m + M}{M}. \tag{18}$$

The vanishing of the frequency ν_2 arises from the fact that in the central force treatment, the relative displacements in the vibration ν_2 are small quantities of a higher order than the second and hence the restoring force is zero in the approximation (15). The forms of the three vibrations are shown in Fig. 3.

(ii) Equilateral triangle

When the three atoms in the molecule are all identical and form an equilateral triangle, equations (17) become, on setting $k_1 = k_2 = k_3 = k$, $\alpha_1 = \alpha_2 = \alpha_3 = 60°$,

$$\lambda_1 = 3\frac{k}{m}, \qquad \lambda_2 = \lambda_3 = \frac{3}{2}\frac{k}{m}. \tag{19}$$

The equality of the frequencies ν_2 and ν_3 illustrates the degeneracy of the normal vibrations due to the symmetry of the molecule. The vibration ν_1 consists of a symmetrical expansion and contraction of the triangle.

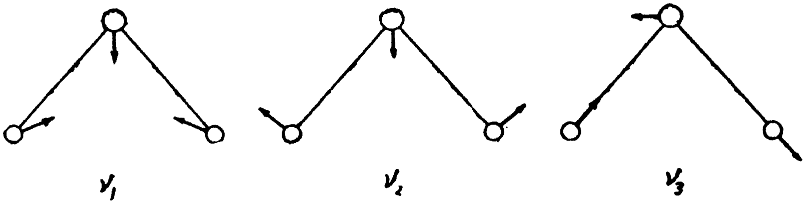

Fig. 2. Vibrations of symmetrical YX_2 molecule

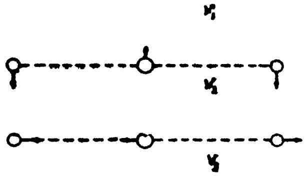

Fig. 3. Vibrations of linear symmetrical YX_2 molecule

B) Valence Force Treatment

The basic idea of the valence force system is that in a molecule a relative displacement of two atoms along the direction of their chemical valence brings about a restoring force which is much greater than that brought about by changes in the angles between valence bonds. Thus in a triatomic molecule in which the chemical bonds are between m_1 and m_2, and between m_2 and m_3, the potential energy is, again on neglecting the cross terms,

$$V = \tfrac{1}{2}\left[k_1 (\delta r_{12})^2 + k_2 (\delta r_{23})^2 + k_\alpha (s\delta\alpha)^2\right], \tag{20}$$

where α is the angle between the directions of the two valence bonds, and s is a quantity having the dimension of length. The validity of the assumption above that the "deformation" force constant k_α is small compared with the valence force constants k_1 and k_2 depends on the smallness of the interaction between m_1 and m_3 compared with those between m_2 and m_3, m_1. That this assumption is justified in the case of many molecules will be seen in Chap. V.

The most extensive study of the normal vibrations of molecules by the valence force treatment is made by Lechner[1]. For the triatomic system, he obtained the following relations among the fundamental frequencies ν_1, ν_2, ν_3.

$$\lambda_1 + \lambda_2 + \lambda_3 = \frac{k}{\mu_1} + \frac{k_2}{\mu_2} + \frac{k_\alpha}{\mu_3},$$

$$\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1 = \frac{k_1 k_2}{\mu_1 \mu_2}\left(1 - \frac{\mu_1\mu_2}{m_2^2}\cos^2\alpha\right) + \left(\frac{k_1}{\mu_1} + \frac{k_2}{\mu_2}\right)\frac{k_\alpha}{\mu_3}$$
$$-\left(\frac{k_1}{r_{23}^2} + \frac{k_2}{r_{12}^2}\right)\frac{k_\alpha s^2 \sin^2\alpha}{m_2^2},$$

$$\lambda_1\lambda_2\lambda_3 = \frac{k_1 k_2 k_\alpha}{\mu_1 \mu_2 \mu_3}\left(1 - \frac{\mu_1\mu_2}{m_2^2}\right), \tag{21}$$

where

$$\frac{1}{\mu_1} = \frac{1}{m_1} + \frac{1}{m_2}, \quad \frac{1}{\mu_2} = \frac{1}{m_2} + \frac{1}{m_3}, \quad \frac{1}{\mu_3} = s^2\left(\frac{1}{\mu_1 r_{12}^2} + \frac{1}{\mu_2 r_{23}^2} - \frac{2\cos\alpha}{m_2 r_{12} r_{23}}\right).$$

Three special cases of the triatomic system are the following:

(i) Symmetrical triangular YX_2

On setting $m_1 = m_3 = m$, $m_2 = M$, $k_1 = k_2 = k$, $r_{12} = r_{23} = s = r$, equations (21) reduce to

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[1] F. Lechner, unpublished *Graz Dissertation;* Wien. Ber. 141, 291, 633, (1932); **Monatsh. f. Chem.** 61, 385, (1932).

$$\lambda_1 + \lambda_2 = k\left(\frac{1}{\mu} + \frac{\cos\alpha}{M}\right) + 2k_\alpha\left(\frac{1}{\mu} - \frac{\cos\alpha}{M}\right),$$

$$\lambda_1\lambda_2 = \frac{2k_\alpha k}{m^2 M}(M + 2m),$$

$$\lambda_3 = k\left(\frac{1}{\mu} - \frac{\cos\alpha}{M}\right), \qquad (22)$$

where

$$\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}.$$

(ii) Non-symmetrical linear XYZ

On setting $\alpha = \pi$, equations (21) reduce to

$$\lambda_1 + \lambda_3 = k_1\left(\frac{1}{m_1} + \frac{1}{m_2}\right) + k_2\left(\frac{1}{m_2} + \frac{1}{m_3}\right),$$

$$\lambda_1\lambda_3 = k_1 k_2 \frac{m_1 + m_2 + m_3}{m_1 m_2 m_3}$$

$$\lambda_2 = \frac{k_\alpha s^2}{r_{12}^2 r_{23}^2}\left(\frac{r_{23}^2}{m_1} + \frac{r_{13}^2}{m_2} + \frac{r_{12}^2}{m_3}\right). \qquad (23)$$

(iii) Linear symmetrical YX_2

Equations (22) become, when $\alpha = \pi$,

$$\lambda_1 = \frac{k}{m},$$

$$\lambda_2 = 2k_\alpha\left(\frac{1}{m} + \frac{2}{M}\right),$$

$$\lambda_3 = k\left(\frac{1}{m} + \frac{2}{M}\right). \qquad (24)$$

The forms of the vibrations of the symmetrical triangular YX_2 are those shown in Fig. 2. That the frequency ν_3 in (22) is independent of k_α means that the vibration ν_3 does not involve a change in the angle α in this approximation. The forms of the vibrations of the linear symmetrical YX_2 are given in Fig. 3. Equations (24) show that the vibration ν_1 consists of a symmetrical vibration of the two X atoms, the frequency being the same as if one X atom were vibrating against the Y atom whose mass is infinite. The vibration ν_3 consists of the vibration of the Y atom against the two X atoms as a rigid group. The vibration ν_2 consists of the vibration of the Y atom perpendicular to the axis of the molecule, or, in the approximation here, a bending of the molecule. In the case of the non-symmetrical linear XYZ molecule, equations (23) show that the vibrations ν_1 and ν_3 involve motions of the three atoms along the axis, while ν_2 is again a bending of the molecule (Fig. 9).

Further examples of the valence force treatment will be found in Chap. V. This method has the advantages (*i*) that the potential function usually contains a relatively small number of constants which can be determined from the observed frequencies, and (*ii*) that the potential so defined can be given a definite physical meaning. There are cases, however, in which the over-simplified valence force potential leads to poor results when compared with the empirical data. In such cases, it is necessary to introduce certain cross terms in the displacements, or start with a more general potential function containing no simplifying assumptions other than what is required by the geometrical symmetry of the molecule, as we shall presently see in the next section.

C) General Force Field Treatment

Here one works with the most general quadratic potential which is consistent with the symmetry of the molecule. Such a potential in general contains a larger number of constants than the number of distinct fundamental frequencies and is hence limited in its usefulness except in a few simple cases when the molecule possesses very high symmetry or shows isotope effect. In the following, we shall only consider the symmetrical YX_2 molecule.

For defining the relative positions of the atoms in the YX_2 molecule, let us choose the following coordinates: q is the relative displacement of the two X atoms along the line X-X; y is the relative displacement of Y from the center of gravity of the X atoms, in the direction of the axis of symmetry; and x is the relative displacement of Y from the c. g. of the X atoms in directions perpendicular to the symmetry axis and in the plane of the molecule. In these coordinates the kinetic energy of vibration is

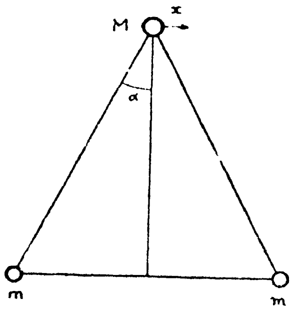

Fig. 4

$$2T = \tfrac{1}{2} m \dot{q}^2 + \frac{2Mm}{S}\left(1 + \frac{M}{S}\cot^2\alpha\right)\dot{x}^2 + \frac{2Mm}{S}\dot{y}^2, \tag{25}$$

where $S=M+2m$. The most general quadratic potential consistent with the symmetry of the molecule, namely, V must be an even function in the coordinate x, is

$$2\,V = A\,q^2 + B\,x^2 + C\,y^2 + 2D\,qy. \tag{26}$$

The determinantal equation gives two vibrations ν_1 and ν_2 which are symmetrical with respect to the symmetry axis and one vibration ν_3 which is antisymmetrical,

$$\begin{aligned} \lambda_1 + \lambda_2 &= \frac{1}{m}\left(2A + \frac{1}{2p}\,C\right), \\ \lambda_1\,\lambda_2 &= \frac{1}{m^2\,p}\,(A\,C - D^2), \\ \lambda_3 &= \frac{B}{2mp\,(1 + p\cot^2\alpha)}\,, \end{aligned} \tag{27}$$

where $p = M/(M+2m)$. The exact forms of these vibrations can be obtained from the transformation equations between the coordinates q, x, y and the normal coordinates X_1, X_2, X_3. By means of (27), these equations can be shown to be

$$\begin{aligned} q &= c_{11}\,X_1 + c_{12}\,X_2, \\ y &= c_{21}\,X_1 + c_{22}\,X_2, \\ x &= \qquad\qquad\quad c_{33}\,X_3. \end{aligned} \tag{28}$$

From these equations it is seen that the forms of vibrations are those shown in Fig. 2. Since there are now four constants A, B, C, D and only three frequencies, additional information is necessary for their determination (see §7 on isotope effects).

For the linear symmetrical YX_2 molecule, equations (27) reduce, on setting $\alpha = \frac{\pi}{2}$ and $D = 0$,

$$\lambda_1 = 2A/m, \quad \lambda_2 = C/2pm, \quad \lambda_3 = B/2pm. \qquad \text{(27a}$$

The connection between the constants A, B, C, D defined in (25) and the constants in a potential including both central and valence forces, namely,

$$2V = k_1[(\delta r_1)^2 + (\delta r_2)^2] + k_2\,(\delta r_3)^2 + k_\alpha\,(r\delta\alpha)^2, \tag{29}$$

where δr_1, δr_2, δr_3 are the changes in the Y-X, Y-X, X-X bond distances respectively, and r the normal X-Y bond distance, is given by the following relations[1]

---

[1] A general force treatment of the YX_2 molecule has been given by Salant and Rosenthal, Phys. Rev. 42, 813, (1932), but the results for the antisymmetrical vibration ν_3 obtained there and the expressions for the isotope shifts of ν_3 are in error through a mistake in the expression for the coordinate x and hence for the constant B.

$$
\begin{aligned}
k_1 &= \tfrac{1}{4} B \csc^2\alpha \, \mathrm{P}, \\
k_2 &= A - \tfrac{1}{4} B \csc^2\alpha \, (1 - \cot^2\alpha) \, \mathrm{P} - \tfrac{1}{4} C \cot^2\alpha, \\
k_\alpha &= [C - B \cot^2\alpha \, P] \csc^2\alpha, \\
D &= \tfrac{1}{4} \cot\alpha \, [B \csc^2\alpha \, P - C],
\end{aligned}
\tag{30}
$$

where

$$P = (1 + p \cot^2\alpha)^{-2}.$$

From these, the results of the valence force treatment (22) can be obtained by setting $k_2=0$, and those of the central force treatment (17) can be obtained by setting $k_\alpha=0$.

It should perhaps be emphasized that while different potential functions naturally lead to different numerical results for a given molecule, certain features such as the general forms and the degeneracy of the normal vibrations depend only on the symmetry properties of the molecule and are entirely independent of the particular choice of the form and the numerical constants of the potential function. For this reason, it is possible to determine these general features for a molecule by considering some extreme form of the potential function, for example, the valence force potential. What is obtained concerning the symmetry properties of the normal vibrations of a molecule in the valence treatment also holds for the central force treatment, and vice versa. Although the actual relative displacements depend on the masses of the atoms and the potential function employed, such qualitative considerations are very useful and form the starting point on which to base a quantitative study of the vibrational spectra of the molecule.

§4. Infrared Absorption Spectra

We shall now investigate the spectrum of a molecule on the basis of the classical theory. According to it, a system (be it an atom or a molecule) is capable of absorbing energy from an incident beam of radiation if the time rate of change of the electric moment of the system does not vanish. Since the distribution of the electric charges in a molecule is a function of the relative coordinates of all the particles (electrons and atomic nuclei), the electric moment will change in general during the vibrations of the molecule. Also the rotation of a molecule in general causes a change in the components of the electric moment along fixed directions in space. There is hence a possibility for the absorption of radiation by a vibrating and rotating molecule.

Consider first a molecule which is not rotating. Its electric moment $\mathfrak{M}$ can be resolved into three components along three mutually perpendicular directions fixed in the molecule (and hence fixed in space also in this case). Each component, say $\mathfrak{M}_\xi$, is a function of the normal coordinates defining the relative positions of the atomic nuclei. For small vibrations, we may expand $\mathfrak{M}_\xi$ in terms of the normal coordinates about the position of equilibrium

$$\mathfrak{M}_\xi = \mathfrak{M}_\xi^\circ + \sum_i \left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0 X_i + \cdots\cdots, \qquad (31)$$

where $\mathfrak{M}_\xi^\circ$ is the ξ-component of the permanent electric moment, *i.e.*, the value of $\mathfrak{M}_\xi$ in the position of equilibrium. Since $\mathfrak{M}_\xi^\circ$ is constant with respect to time, it plays no part in the absorption and emission of radiation. Since by equation (10), $X_i = A_i \cos\,(2\pi\nu_i t - \varepsilon_i)$, $\mathfrak{M}_\xi$ contains the periodic terms with the frequencies $\nu_1, \nu_2, \cdots\cdots \nu_n$ of the normal vibrations of the molecule. Hence in a first approximation in which only the linear terms in the normal coordinates are considered in the above expansion (*i.e.*, when only the so-called dipole radiation is considered), the molecule can only absorb radiations of frequencies $\nu_1, \nu_2 \cdots\cdots \nu_n$. It does not follow, however, that all the normal vibrations are active in absorption. If for a vibration ν_i all the coefficients $\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0$, $\xi = \xi, \eta, \zeta$, vanish, then the frequency ν_i will not appear in the spectrum. The question as to whether a particular vibration is active must be answered by a close examination of the symmetry properties of the molecule and the vibration ν_i. We shall come back to this in §6, and also in Chap. V when dealing with the individual molecules.

Next let us consider a molecule which is vibrating and rotating at the same time. Let the orientation of the molecule be defined by means of the direction cosines of a set of axes ξ, η, ζ fixed in the molecule with respect to another set x, y, z fixed in space. The component of the electric moment along a fixed direction, say the x-axis, is given by

$$\mathfrak{M}_x = \mathfrak{M}_\xi \cos \widehat{\xi x} + \mathfrak{M}_\eta \cos \widehat{\eta x} + \mathfrak{M}_\zeta \cos \widehat{\zeta x}, \qquad (32)$$

in which $\mathfrak{M}_\xi$, $\mathfrak{M}_\eta$, $\mathfrak{M}_\zeta$ are given by expressions of the form (31). Hence one has

$$\mathfrak{M}_x = \sum_\xi \mathfrak{M}^\circ \cos \widehat{\xi x} + \sum_{\xi,i} A_i \left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0 \cos \widehat{\xi x} \cos\,(2\pi\nu_i t - \varepsilon_i), \qquad (32a)$$

in which the summation ξ is over $\xi = \xi, \eta, \zeta$. Since the angles $\widehat{\xi x}, \widehat{\eta x}, \cdots$

etc. are periodic in time if the rotation of the molecule is uniform, one may write $\cos \widehat{\xi x} = \cos 2\pi \nu_{\xi x} t$, etc., where $\nu_{\xi x}$ is a frequency. On substituting such expressions into (32a), it is seen that in general $\mathfrak{M}_x$, $\mathfrak{M}_y$, $\mathfrak{M}_z$ contain periodically varying terms with the frequencies $\nu_{\xi x}$, ν_i, $\nu_i \pm \nu_{\xi x}$, $\xi = \xi, \eta, \zeta$, where $x = x, y, z$. The absorption frequencies $\nu_{\xi x}$ form the the pure rotational spectrum. For this not to vanish, the components of the permanent electric moment must not all vanish. The frequencies ν_i, $\nu_i \pm \nu_{\xi x}$ form the so-called vibration-rotational spectrum. For the particular vibration-rotational band with frequencies ν_i, $\nu_i \pm \nu_{\xi x}$ not to vanish, the coefficients $\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0$, $\left(\frac{\partial \mathfrak{M}_\eta}{\partial X_i}\right)_0$, $\left(\frac{\partial \mathfrak{M}_\zeta}{\partial X_i}\right)_0$ must not all vanish, *i.e.*, the vibration must involve a change of the electric moment of the molecule.

To make the situation clearer, let us suppose the molecule to be a symmetrical top possessing a symmetry axis ζ and two equal moments of inertia about two perpendicular axes normal to the ζ axis. Imagine at a certain instant the ζ-axis coincides with the space z-axis, and consider a vibration ν_i which is accompanied by a change of the electric moment along the symmetry axis alone, *i.e.*, $\left(\frac{\partial \mathfrak{M}_\zeta}{\partial X_i}\right)_0 \neq 0$ and $\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right) = \left(\frac{\partial \mathfrak{M}_\eta}{\partial X_i}\right)_0 = 0$. We shall called such a vibration a "parallel" vibration. Now in the rotation of the molecule about the symmetry axis, the components of the electric moment are evidently

$$\mathfrak{M}_x = \mathfrak{M}_y = 0, \quad \mathfrak{M}_z = A_i \left(\frac{\partial \mathfrak{M}_\zeta}{\partial X_i}\right)_0 \cos(2\pi \nu_i t - \varepsilon_i). \tag{33}$$

Hence the absorption spectrum contains only the frequency ν_i. If the molecule rotates uniformly about an axis perpendicular to the symmetry axis with a frequency ν_r, then

$$\begin{aligned} \left.\begin{matrix}\mathfrak{M}_x \\ \mathfrak{M}_y\end{matrix}\right\} &= \left[\mathfrak{M}^\circ_\zeta + A_i \left(\frac{\partial \mathfrak{M}_\zeta}{\partial X}\right)_0 \cos(2\pi \nu_i t - \varepsilon_i)\right] \sin 2\pi \nu_r t \cdot \left\{\begin{matrix}\sin \varphi \\ \cos \varphi\end{matrix}\right. \\ \mathfrak{M}_z &= \left[\mathfrak{M}^\circ_\zeta + A_i \left(\frac{\partial \mathfrak{M}_\zeta}{\partial X_i}\right)_0 \cos(2\pi \nu_i t - \varepsilon_i)\right] \cos 2\pi \nu_r t, \end{aligned} \tag{34}$$

in which φ is the angle between the axis of rotation and the x-axis. It is seen that now the spectrum contains the frequencies ν_r, $\nu_i \pm \nu_r$. The frequencies ν_r's give the pure rotational spectrum, while the frequencies $\nu_i \pm \nu_r$ form the vibration-rotational band. On combining this with (33), one finds that the band contains the frequencies ν_i and $\nu_i \pm \nu_r$.

If in the vibration ν_i the direction of the change of the electric moment is perpendicular to the symmetry axis, say along the ξ-axis, then $\left(\frac{\partial\mathfrak{M}_\xi}{\partial X_i}\right)_0 \neq 0$, and $\left(\frac{\partial\mathfrak{M}_\eta}{\partial X_i}\right)_0 = \left(\frac{\partial\mathfrak{M}_\zeta}{\partial X_i}\right)_0 = 0$. We shall call such a vibration a "perpendicular" vibration. In rotations about the symmetry axis, one has

$$\mathfrak{M}_z = \mathfrak{M}^\circ_\zeta, \quad \left.\begin{matrix}\mathfrak{M}_x\\ \mathfrak{M}_y\end{matrix}\right\} = A_i\left(\frac{\partial\mathfrak{M}_\xi}{\partial X_i}\right)_0 \cos 2\pi\nu_i t \cdot \left\{\begin{matrix}\cos 2\pi\nu_r t\\ \sin 2\pi\nu_r t\end{matrix}\right. . \tag{35}$$

If the molecule rotates about the ξ-axis, one obtains

$$\begin{aligned}\mathfrak{M}_z &= \mathfrak{M}^\circ_\zeta \cos 2\pi\nu_r t,\\ \left.\begin{matrix}\mathfrak{M}_x\\ \mathfrak{M}_y\end{matrix}\right\} &= \left[\mathfrak{M}^\circ_\zeta \sin 2\pi\nu_r t + A_i\left(\frac{\partial\mathfrak{M}_\xi}{\partial X_i}\right)\cos 2\pi\nu_i t\right] \cdot \left\{\begin{matrix}\sin \widehat{\xi x}\\ \sin \widehat{\xi y}\end{matrix}\right. ,\end{aligned} \tag{36}$$

while for rotations about the η-axis,

$$\begin{aligned}\left.\begin{matrix}\mathfrak{M}_x\\ \mathfrak{M}_y\end{matrix}\right\} &= \left[\mathfrak{M}^\circ_\zeta \sin 2\pi\nu_r t + A_i\left(\frac{\partial\mathfrak{M}_\xi}{\partial X_i}\right)_0 \cos 2\pi\nu_r t \cdot \cos 2\pi\nu_i t\right] \cdot \left\{\begin{matrix}\sin \widehat{\eta x}\\ \sin \widehat{\eta y}\end{matrix}\right. ,\\ \mathfrak{M}_z &= \mathfrak{M}^\circ_\zeta \cos 2\pi\nu_r t + A_i\left(\frac{\partial\mathfrak{M}_\xi}{\partial X_i}\right)_0 \sin 2\pi\nu_r t \cdot \cos 2\pi\nu_i t.\end{aligned} \tag{37}$$

It is seen that the spectrum now consists of a pure rotational spectrum with the frequencies ν_r's, and a vibration-rotational band with the frequencies ν_i and $\nu_i \pm \nu_r$.

In the classical theory, the molecules can rotate with all frequencies continuously distributed according to the Maxwell-Boltzmann law. The general appearance of a vibration-rotational band is hence something like that shown in Fig. 5. The frequencies $\nu_i - \nu_r$, ν_i, $\nu_i + \nu_r$ are called the *P, Q, R* branches of the band respectively. The continuous distribution of the rotational frequencies according to this classical theory is in complete disagreement with the experimental results which show that the various branches contain a number of discrete lines. The explanation is furnished by the quantum theory,

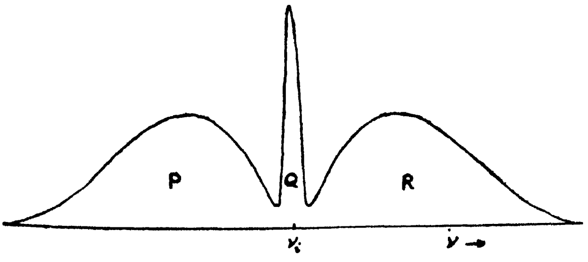

Fig. 5. Contour of vibration-rotational bands of linear molecules

as shown in Chap. IV. We shall now consider two special cases of the symmetrical top.

(*i*) A linear molecule containing more than two atoms.

In this case, the molecule can only rotate about axes normal to the line of atoms and the rotation about the line of atoms is not excited at ordinary temperatures.[1] Hence in a parallel vibration, only the frequencies $\nu_i \pm \nu_r$, but not ν_r, will appear in the spectrum and hence the *Q* branch is absent. In a perpendicular vibration, however, all the *P, Q, R* branches are present.

(*ii*) A diatomic molecule.

In this case it is not possible for the electric moment to be perpendicular to the axis of the molecule. Hence there is only the parallel type band. The *Q* branch is again absent for the same reason as given in (*i*).

It appears from the above discussion that in the spectrum of a molecule, only the fundamental frequencies of the normal vibrations may appear. By taking into consideration the fact that the vibrations are not exactly simple harmonic, it is possible to allow for the presence of harmonic bands. For example, the coordinate *X* should be expressed in general in a Fourier series

$$X_i = \sum_m A_{im} \cos (2\pi m \nu_i t - \varepsilon_{im}). \tag{38}$$

Substitution of this into (31) shows that the spectrum may also contain the frequencies $2\nu_i$, $3\nu_i$, ... etc. Whether any particular harmonic $n\nu_i$ appears or not depends on the vanishing or non-vanishing of the corresponding coefficient A_{in}. It will be shown in §6 that while the numerical values of these coefficients cannot be determined without a detailed knowledge of the structure of the molecule, the vanishing or non-vanishing of them can be determined from a consideration of the symmetry properties of the molecule and the normal vibrations alone. We shall return to this question in §6.

§5. Raman Effect

The theory of Rayleigh scattering, namely, the scattering of radiation of the same frequency as that of the incident radiation by molecules, is well known. In brief, it is as follows: The atom or molecule is polarized under the action of the electric field of the incident radiation and an electric moment is induced in the atom or molecule, which has the same frequency ν_0 as the incident radiation. This induced electric moment varying with the frequency ν_0 radiates energy in the form of radiation of frequency ν_0 according to the laws of electrodynamics. The intensities of the "scattered" radiations in different directions relative to those of the electric field of the incident radiation are determined by the values of the components of the induced electric moment in different directions.

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[1] The explanation of the non-excitation of the rotation about the line of atoms is furnished by the quantum theory. According to it, the energy quantum of rotation is $h^2/8\pi^2 I$, where I is the moment of inertia about the axis of rotation. For the rotation about the line of centers, I is so small that the energy quantum $h^2/8\pi^2 I$ is very large compared with kT at ordinary temperatures.

The discovery of the Raman effect consists in the observation that in addition to the frequency ν_0, the scattered radiations contain other frequencies whose differences with ν_0 correspond to the vibrational and the rotational frequencies of the scattering molecules[1]. In this section, we shall give a discussion of the Raman effect on the basis of the classical theory. The modifications introduced by the quantum theory will be given in Chap. III. A thorough discussion of this subject can be found in the works of Placzek[2], Stuart[3] and of Teller[4], and to these the reader must be referred for details.

Consider a molecule in general. When an electric field of intensity $\mathcal{E}$ is applied in different directions in turn, the induced electric moment is in general different because of the difference in the ease with which the molecule is polarized in different directions. The polarizability α which connects the induced electric moment $\mathfrak{M}$ and the inducing electric field $\mathcal{E}$ by the definitional equation

$$\mathfrak{M} = \alpha\,\mathcal{E} \tag{39}$$

is in general a tensor having the components α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{yz}, α_{zx}, and can be represented by an ellipsoid. The above equation is equivalent to the following set of equations

[1] C. V. Raman, Ind. Jour. Phys. 2, 387, (1928); For discussions of the experimental methods and results, see Kohlrausch, *Der Smekal-Raman Effekt*, (1931), and *Ergänzungsband*, (1938).

[2] G. Placzek, Leipziger Vorträger, (1931); chapter in Marx: *Handbuch der Radiologie*, Band VI/2, (1934).

[3] H. A. Stuart, *Molekülstruktur*, (1934).

[4] E. Teller, chapter in Eucken-Wolf: *Hand-und Jahrbuch der chemischen Physik*, Band 9/II, (1934).

$$\begin{aligned}\mathfrak{M}_\xi &= \alpha_{\xi\xi}\,\mathfrak{E}_\xi + \alpha_{\xi\eta}\,\mathfrak{E}_\eta + \alpha_{\xi\zeta}\,\mathfrak{E}_\zeta\,,\\ \mathfrak{M}_\eta &= \alpha_{\eta\xi}\,\mathfrak{E}_\xi + \alpha_{\eta\eta}\,\mathfrak{E}_\eta + \alpha_{\eta\zeta}\,\mathfrak{E}_\zeta\,,\\ \mathfrak{M}_\zeta &= \alpha_{\zeta\xi}\,\mathfrak{E}_\xi + \alpha_{\zeta\eta}\,\mathfrak{E}_\eta + \alpha_{\zeta\zeta}\,\mathfrak{E}_\zeta\,. \end{aligned} \tag{39a}$$

If in the molecule a set of axes ξ, η, ζ which are the principal axes of the ellipsoid α be chosen as the coordinate axes, then the components $\alpha_{\xi\eta}$, $\alpha_{\eta\zeta}$, $\alpha_{\zeta\xi}$ vanish. These principal axes are in general the same as the principal axes of moment of inertia of the molecule, except in the case of molecules in which one or more of a number of identical atoms is replaced by its isotopes.[5]

Consider a molecule at rest, whose principal values of the polarizability are $\alpha_{\xi\xi}$, $\alpha_{\eta\eta}$, $\alpha_{\zeta\zeta}$, and let a beam of linearly polarized radiation fall on the molecule along the ζ-axis, with the electric vector $\mathfrak{E}$ making an angle ϑ with the ξ-axis. The components of the induced electric moment are, according to (39a),

$$\mathfrak{M}_\xi = \alpha_{\xi\xi}\,\mathfrak{E}_\xi = \mathfrak{E}\,\alpha_{\xi\xi}\cos\vartheta,\quad \mathfrak{M}_\eta = \mathfrak{E}\,\alpha_{\eta\eta}\sin\vartheta,\quad \mathfrak{M}_\zeta = 0. \tag{40}$$

The direction of the induced electric moment $\mathfrak{M}$ therefore makes an angle $\tan^{-1}\left(\frac{\alpha_{\eta\eta}\sin\vartheta}{\alpha_{\xi\xi}\cos\vartheta}\right)$ with the ξ-axis. Hence unless $\alpha_{\xi\xi}=\alpha_{\eta\eta}$, the directions of $\mathfrak{M}$ and $\mathfrak{E}$ are different in general. As a result of this, the scattered radiation is no longer polarized in the plane making the angle ϑ with the $\xi-\zeta$ plane as the incident radiation. The ratio of the intensity of the scattered radiation polarized in directions perpendicular to this plane to the intensity of the radiation polarized in this plane is seen to be

$$\varrho = \frac{|\alpha_{\xi\xi}-\alpha_{\eta\eta}|^2\sin^2\vartheta\cos^2\vartheta \text{ [6]}}{|\alpha_{\xi\xi}\cos^2\vartheta+\alpha_{\eta\eta}\sin^2\vartheta|^2}\,. \tag{41}$$

This ratio is defined as the degree of depolarization and it is seen that $\varrho = 0$ if $\alpha_{\xi\xi}=\alpha_{\eta\eta}$; that is, the scattered radiation will be polarized if the molecule is isotropic about the ζ-axis. Similarly, it can be shown that unless α is a sphere, i.e., $\alpha_{\xi\xi}=\alpha_{\eta\eta}=\alpha_{\zeta\zeta}$, the scattered radiation is in general partially depolarized, in the sense that the electric intensity of the radiation scattered from an incident beam of polarized radiation has a different direction than that of the incident radiation. The frequency of the scattered radiations is, as long as the molecule is fixed, the same as that of the incident beam, as can be seen by putting $\mathcal{E} = \mathcal{E}_0 \sin 2\pi\nu_0 t$ in (40). This accounts for the Rayleigh scattering.

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[5] The polarizability is essentially determined by the electronic structure of the molecule and is hence not effected by an isotope replacement. The moments of inertia, on the other hand, will be changed since they depend on the masses of the atoms.

[6] When one is dealing not with one single molecule but with a large number of molecules oriented in different directions at random, it is necessary to average the intensities of the scattered radiations over all possible directions of the molecule relative to the direction of the inducing electric field $\mathfrak{E}$. The above discussion is used only in order to simplify the situation.

Let us next suppose the molecule to be rotating uniformly with the frequency ν_r about the ζ-axis which is taken as the z-axis of a system of axes x, y, z fixed in space. Let the electric field $\mathcal{E} = \mathcal{E}_0 \sin 2\pi\nu_0 t$ of the incident radiation be along the x-axis. The components of the induced electric moment along the x and the y axes are (Fig. 6),

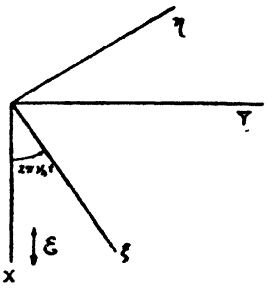

Fig. 6

$$\mathfrak{M}_x = \mathfrak{M}_\xi \cos 2\pi\nu_r t - \mathfrak{M}_\eta \sin 2\pi\nu_0 t,$$

$$\mathfrak{M}_y = \mathfrak{M}_\xi \sin 2\pi\nu_r t + \mathfrak{M}_\eta \cos 2\pi\nu_r t. \tag{42}$$

Since

$$\mathfrak{M}_\xi = \alpha_{\xi\xi}\, \mathcal{E} \cos 2\pi\nu_r t, \qquad \mathfrak{M}_\eta = -\alpha_{\eta\eta}\, \mathcal{E} \sin 2\pi\nu_r t, \tag{43}$$

one obtains

$$\mathfrak{M}_x = \tfrac{1}{2} \mathcal{E}_0 [(\alpha_{\xi\xi} + \alpha_{\eta\eta}) + (\alpha_{\xi\xi} - \alpha_{\eta\eta}) \cos 2\pi(2\nu_r)t] \sin 2\pi\nu_0 t,$$

$$\mathfrak{M}_y = \tfrac{1}{2} \mathcal{E}_0 (\alpha_{\xi\xi} - \alpha_{\eta\eta}) \sin 2\pi(2\nu_r)t \cdot \sin 2\pi\nu_0 t. \tag{42a}$$

From these expressions, it is seen that $\mathfrak{M}_x$, $\mathfrak{M}_y$ and hence the scattered radiations have the frequencies ν_0 and $\nu_0 \pm 2\nu_r$. The former is the Rayleigh scattering, while the latter with the frequencies $\nu_0 \pm 2\nu_r$ are the pure rotational Raman lines. These rotational Raman effect is present only when the molecule is not isotropic about the ζ-axis, i.e., when $\alpha_{\xi\xi} \neq \alpha_{\eta\eta}$. This is already clear from (41), since if the polarizability ellipsoid is one of revolution about the ζ-axis, the direction of the induced electric moment will always coincide with that of the inducing field $\mathcal{E}$ and the rotation of the molecule about the ζ-axis cannot affect the direction of the induced electric moment. (When one considers the rotation of the molecule about any arbitrary axis instead of the ζ-axis, then the condition for the rotational Raman effect to be absent is that the polarizability ellipsoid is a sphere).

It is also seen from (42a) that the rotation introduces the frequency $2\nu_r$ instead of ν_r as in the vibration-rotational band in the absorption spectrum (§4). This is due to the fact that the polarizability ellipsoid and hence the induced electric moment resume their original values upon a rotation through π, and in 2π, the polarizability completes two cycles. Here one is dealing with a tensor, while in absorption one is dealing with a vector.

From this simple example, it follows that the rotational Raman lines are completely depolarized, since the intensities of the x and the y components are the same. Since the rotational frequency of the molecule can take on all values according to the classical theory, the rotational Raman spectrum consists of two branches on both sides of the Rayleigh line ν_0. The high frequency branch is called the *S* branch and the low frequency branch the *O* branch. The general appearance will be somewhat like that shown in Fig. 5.

For the vibrational Raman effect, we shall again assume that the polarizability α, which is a function of the relative coordinates defining the positions of the atoms, can be expanded about the position of equilibrium in terms of the normal coordinates; *i.e.*, for each component α_{ij} we have an expansion of the form

$$\alpha_{\xi\xi} = (\alpha_{\xi\xi})^\circ + \sum_i \left(\frac{\partial \alpha_{\xi\xi}}{\partial X_i}\right)_\circ X_i + \cdots\cdots \tag{44}$$

in which $(\alpha_{\xi\xi})^\circ$ is the $\xi\xi$-component of the polarizability of the molecule in the position of equilibrium, and $\left(\frac{\partial \alpha_{\xi\xi}}{\partial X_i}\right)_\circ X_i$ is the change in the $\xi\xi$ -component due to the normal vibration ν_i. Suppose first the molecule is not rotating. Substitution of this and similar expressions into (39a) gives

$$\mathfrak{M}_\xi = \sum_j \mathcal{E}_j (\alpha_{\xi j})^\circ + \sum_j \sum_i \mathcal{E}_j \left(\frac{\partial \alpha_{\xi j}}{\partial X_i}\right)_\circ X_i, \tag{45}$$

in which j is summed over $j=\xi,\ \eta,\ \zeta$. On putting $\mathcal{E} = \mathcal{E}_0 \sin 2\pi\nu_0 t$, it is seen that $\mathfrak{M}_\xi$, $\mathfrak{M}_\eta$, $\mathfrak{M}_\zeta$ depend on time through terms containing the factors $\cos 2\pi\nu_0 t$, $\cos 2\pi(\nu_0 \pm \nu_i)t$ and $\sin 2\pi(\nu_0 \pm \nu_i)t$. Thus in the approximation in which only terms linear in the coordinates X_i are considered, and the X's are supposed to be simple harmonic, the scattered radiations have the frequencies ν_0 and $\nu_0 \pm \nu_i$, where $i=1, 2, \ldots .n$. (see below). The frequency ν_0 is once more the frequency of the Rayleigh scattering; the $\nu_0 \pm \nu_i$ are the vibrational Raman lines. The high frequency $\nu_0 + \nu_i$ is called the anti-Stokes line, and the low frequency $\nu_0 - \nu_i$ the Stokes line.

Finally let us consider the simultaneous vibration and rotation of a molecule. For this purpose, we have to consider the components of the induced electric moment along the space axes x, y, z. On substituting (45) into (32), one obtains

$$\mathfrak{M}_x = \sum_{\xi}\left[\sum_{j} \mathcal{E}_j (\alpha_{\xi j})^\circ\right]\cos\widehat{\xi x} + \sum_{\xi}\left[\sum_{i}\sum_{j} \mathcal{E}_j \left(\frac{\partial \alpha_{\xi j}}{\partial X_i}\right)_\circ X_i\right]\cos\widehat{\xi x}, \tag{46}$$

in which ξ is summed over ξ, η, ζ. Similar expressions hold for $\mathfrak{M}_y$ and $\mathfrak{M}_z$. As an illustration of the result represented by (46), let us return to the simple situation in Fig. 6. Suppose the vibration ν_i to be such that

$$\alpha'_{\xi\xi} = \left(\frac{\partial \alpha_{\xi\xi}}{\partial X_i}\right)_\circ \neq 0, \qquad \alpha'_{\eta\eta} = \left(\frac{\partial \alpha_{\eta\eta}}{\partial X_i}\right)_\circ \neq 0,$$

and all the other coefficients vanish. In this case, one obtains

$$\begin{aligned}
\mathfrak{M}_x = \frac{1}{4}\,\mathcal{E}_\circ \Big\{ &(\alpha_{\xi\xi} + \alpha_{\eta\eta}) \sin 2\pi\nu_\circ t + (\alpha_{\xi\xi} - \alpha_{\eta\eta}) [\sin 2\pi(\nu_\circ + 2\nu_r)\,t \\
&+ \sin 2\pi(\nu_\circ - 2\nu_r)\,t] \Big\} \\
&+ \frac{1}{4} A_i\, \mathcal{E}_\circ \Big\{ (\alpha'_{\xi\xi} + \alpha'_{\eta\eta}) [\sin 2\pi(\nu_\circ + \nu_i)\,t + \sin 2\pi(\nu_\circ - \nu_i)\,t] \\
&+ (\alpha'_{\xi\xi} - \alpha'_{\eta\eta}) [\cos 2\pi(\nu_\circ + \nu_i + 2\nu_r)\,t - \cos 2\pi(\nu_\circ - \nu_i + 2\nu_r)\,t \\
&+ \cos 2\pi(\nu_\circ + \nu_i - 2\nu_r)\,t - \cos 2\pi(\nu_\circ - \nu_i - 2\nu_r)\,t] \Big\}, \\
\mathfrak{M}_y = \frac{1}{4}\,\mathcal{E}_\circ \Big\{ &(\alpha_{\xi\xi} - \alpha_{\eta\eta}) [\cos 2\pi(\nu_\circ + 2\nu_r)\,t - \cos 2\pi(\nu_\circ - 2\nu_r)\,t] \Big\} \\
&+ \frac{1}{4} A_i\, \mathcal{E}_\circ \Big\{ (\alpha'_{\xi\xi} - \alpha'_{\eta\eta}) [\cos 2\pi(\nu_\circ + \nu_i + 2\nu_r)\,t - \cos 2\pi(\nu_\circ - \nu_i + 2\nu_r)\,t \\
&+ \cos 2\pi(\nu_\circ + \nu_i - 2\nu_r)\,t - \cos 2\pi(\nu_\circ - \nu_i - 2\nu_r)\,t] \Big\}.
\end{aligned} \tag{47}$$

The terms in $\mathcal{E}_\circ$ give the Rayleigh scattering and the pure rotational Raman scattering $\nu_\circ \pm 2\nu_r$ as in (42a). The terms in $A_i\,\mathcal{E}_\circ$ give the frequencies $\nu_\circ \pm \nu_i$, $\nu_\circ \pm \nu_i \pm 2\nu_r$. The frequencies $\nu_\circ - \nu_i$ and $\nu_\circ + \nu_i$ are those of the Stokes and anti-Stokes vibrational Raman lines. The frequencies $\nu_\circ \pm \nu_i \pm 2\nu_r$ give rise to the rotational "wings" on the two sides of each of the lines $\nu_\circ \pm \nu_i$. It is seen from these expressions that the rotational lines $\nu_\circ \pm \nu_i \pm 2\nu_r$ are completely depolarized, since the intensities of the x and the y components are equal. It is also seen that these lines will vanish if $\alpha'_{\xi\xi} = \alpha'_{\eta\eta}$, *i.e.*, if the change of the polarizability is isotropic about the ζ-axis. The intensities of the vibrational Raman lines $\nu_0 \pm \nu_i$ depenl, however, on $\alpha'_{\xi\xi} + \alpha'_{\eta\eta}$ and hence will not vanish unless either $\alpha'_{\xi\xi} = \alpha'_{\eta\eta} = 0$, or $\alpha'_{\xi\xi} = -\alpha'_{\eta\eta}$. If in the vibration ν_i all the components of the change of the polarizability vanish, namely, $\alpha'_{\xi\xi} = \alpha'_{\eta\eta} = \alpha'_{\zeta\zeta} = \alpha'_{\xi\eta} = \alpha'_{\eta\zeta} = \alpha'_{\zeta\xi} = 0$, then the vibrational and also the vibration-rotational Raman lines will not appear in the Raman spectrum.

The question as to whether any particular vibration will appear in the Raman spectrum, and if so, what is the polarization character of the scattered radiation, must be answered by a close examination of the coefficients, $\alpha'_{\xi\xi}$, $\alpha'_{\eta\eta}$, $\alpha'_{\zeta\zeta}$, $\alpha'_{\xi\eta}$ $\alpha'_{\eta\zeta}$, $\alpha'_{\zeta\xi}$. In general the vanishing or non-vanishing of these coefficients can be determined from a study of the symmetry properties of the molecule and of its vibrations. We shall discuss this in the following section.

The above classical theory is satisfactory in accounting for the various frequency shifts in the Raman spectrum. There is one serious difficulty, however, when one considers the intensities of the Raman lines. According to the theory, the amplitudes of the electric moments with the frequencies $\nu_0 + \nu_i$ and $\nu_0 - \nu_i$ are the same, and hence the intensities of the Stokes and the anti-Stokes lines should be the same. Experimentally it is found that in all cases the Stokes line $\nu_0 - \nu_i$ is by far very much more intense than the anti-Stokes line $\nu_0 + \nu_i$. In fact, the latter is observed only in the case of low values of the vibrational frequency ν_i (below ~ 500 cm^{-1}) and then only with low intensities. This great difference between the Stokes and the anti-Stokes lines cannot be understood on the classical theory, but is readily explained in the quantum theory. We shall come back to this question in Chap. III, §2, B.

§6. Symmetry Properties of Vibrations and Selection Rules

It is shown in §1 that the normal vibrations of a molecule are given by the determinantal equation (8) in general. It can be shown that in molecules possessing certain elements of symmetry, the determinant in (8) can be reduced into one which consists of a number of sub-determinants along the principal diagonal, all elements outside these sub-determinants being zero. The possibility of such a reduction depends only on the symmetry properties of the molecule (that is, the symmetry in the geometry and the masses of the atoms and the potential function), but is independent of the particular choice of the form of the potential function or the numerical value of the constants in the potential function. Consider for example the symmetrical YX_2 molecule. It is seen from equations (17), (22) and (27) that in all the central force, valence force and the general force field treatments, the determinant is reducible to one linear and quadratic factor. The element of symmetry is in this case the axis bisecting the apex angle of the isoceles triangle. The quadratic factor gives two vibrations which are symmetrical with respect to this axis, while the linear factor gives one vibration which is antisymmetrical with respect to this axis. It will be seen in Chap. V that irrespective of the force system employed, the determinantal equation for a symmetrical pyramidal YX_3 molecule is reducible to three quadratic factors two of which are identical. The single quadratic factor gives two vibrations that are symmetrical with respect to the axis of the pyramid; the repeated quadratic factors give a pair of doubly degenerate vibrations.

In the case of most of the simpler molecular models, it is usually an easy matter to determine, without actually solving the determinantal equation, the number of normal vibrations having a given symmetry property. It is simply the number of independent, subject to the prescribed symmetry, coordinates necessary for completely defining the relative positions of the atoms. Thus for the symmetrical YX_2 molecule, the number of these coordinates for the symmetrical (with respect to the axis of symmetry) vibrations is two, for example, the Y-X bond distance, which is the same for the two bonds, and the angle between the two bonds. The number of coordinates for the antisymmetrical vibrations is one, namely, either one bond distance (the other is fixed by the requirement that $\delta r_1 = -\delta r_2$), or the displacement x defined in Fig. 4 and equation (26). Hence there are two symmetrical vibrations and one antisymmetrical vibration.

As another example, let us take a molecule of the ethylene type Y_2X_4 and choose a coordinate system with its origin at the center of gravity of the molecule, the z-axis being along the Y-Y bond and the x-axis in the plane of the molecule (Fig. 7). Let us inquire about the number of vibrations that are (*i*) symmetrical with respect to all the three coordinate planes, and (*ii*) symmetrical with respect to the y-z and z-x planes but antisymmetrical with respect to the x-y plane. For (*i*), three coordinates are necessary, for example, the Y-X bond distance (which is the same for all the four bonds), the angle between two adjacent Y-X bonds, and the Y-Y bond distance. For (*ii*), the first two of these are sufficient since

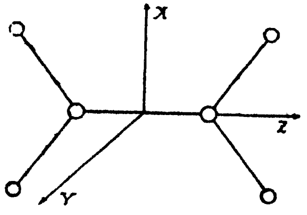

Fig. 7

the Y-Y distance remains unchanged in the antisymmetrical vibration. Hence there are three totally symmetrical vibrations and two that are antisymmetrical with respect to the plane perpendicular to the Y-Y axis. The forms of these and the other normal vibrations of the Y_2X_4 molecule are given in Fig. 35 in Chap. V.

While it is always possible to determine the number of vibrations of various symmetry properties either by the above argument or by actually solving the determinantal equation, the latter procedure entails lengthy calculations in the case of the more complicated molecules. In such cases, the elegant method of the group theory can be applied.[1] According to the group theory, the problem of finding the number of vibrations of different symmetry properties is reduced to that of finding the number of times the various irreducible representations appear in the group of all the symmetry operations. Considerations of the symmetry properties of the molecule alone enable a determination to be made of the number of vibrations of various symmetry properties. An account of the application of the group theory to the problem of molecular vibrations has been given by Rosenthal and Murphy[2], and the results for a number of molecular models have been tabulated by them and by Placzek[3], and Wilson[4]. The reader must be referred to these and other papers for an exposition of this powerful method. Here we shall be contented with the results that are obtained by means of the group theory.

We shall now consider the relations between the symmetry properties of the vibrations of a molecule and the selection rules in the absorption and the Raman spectra. Consider first the absorption spectrum of a molecule. It has been shown in §4 that the vibration ν_i is active in absorption or emission only if the coefficients $\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0$, $\xi = \xi, \eta, \zeta$ do not all vanish. If in the vibration ν_i the molecule remains symmetrical with respect to the y-z plane, it follows that the x-component of the change of the electric moment is zero, *i.e.*, $\left(\frac{\partial \mathfrak{M}_x}{\partial X_i}\right)_0 = 0$. If $\left(\frac{\partial \mathfrak{M}_y}{\partial X_i}\right)_0 \neq 0$ and also $\left(\frac{\partial \mathfrak{M}_z}{\partial X_i}\right)_0 \neq 0$, then the radiation emitted or absorbed will be polarized in the y-z plane. If in the vibration ν_i the molecule remains symmetrical with respect to the y-z and the z-x planes, then $\left(\frac{\partial \mathfrak{M}_x}{\partial X_i}\right)_0 = \left(\frac{\partial \mathfrak{M}_y}{\partial X_i}\right)_0 = 0$. If $\left(\frac{\partial \mathfrak{M}_z}{\partial X_i}\right)_0$ does not vanish, the radiation emitted or absorbed will be linearly polarized, the electric intensity being along the z-axis.[5] If in the vibration ν_i the molecule remains symmetrical with respect to all the three coordinate planes or to its center of symmetry, then $\left(\frac{\partial \mathfrak{M}_x}{\partial X_i}\right)_0 = \left(\frac{\partial \mathfrak{M}_y}{\partial X_i}\right)_0 = \left(\frac{\partial \mathfrak{M}_z}{\partial X_i}\right)_0 = 0$ and all components of the electric moment with the frequency ν_i vanish and the vibration is inactive. Thus an examination of the symmetry properties of the normal vibrations will enable one to determine the optical activities and also the polarization state of the radiation emitted or absorbed.

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[1] E. Wigner, Gött. Nach. P. 133, (1930).

[2] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. 8, 317, (1936).

[3] G. Placzek, *Handbuch der Radiologie*, Bd. 6/II, (1934).

[4] E. B. Wilson, jr. Jour. Chem. Phys. 2, 432, (1934).

As an illustration, let us take the linear symmetrical YX_2 molecule (Fig. 3), and for the three normal vibrations we shall choose the following coordinates which are proportional to the normal coordinates: the vibration ν_1 is described by the relative displacement q of the two X atoms; ν_2 is described by the displacement r of the Y atom from the line joining the two X atoms; and ν_3 is described by the displacement z of the Y atom from the center of gravity of the two X atoms, in direction along the axis of the molecule. It is clear from Fig. 3 that

$$\left(\frac{\partial \mathfrak{M}_z}{\partial q}\right)_0 = 0, \quad \left(\frac{\partial \mathfrak{M}_z}{\partial r}\right)_0 = 0, \quad \left(\frac{\partial \mathfrak{M}_z}{\partial z}\right)_0 \neq 0,$$
$$\left(\frac{\partial \mathfrak{M}_{x,y}}{\partial q}\right)_0 = 0, \quad \left(\frac{\partial \mathfrak{M}_{x,y}}{\partial r}\right) \neq 0, \quad \left(\frac{\partial \mathfrak{M}_{x,y}}{\partial z}\right) = 0. \tag{48}$$

From these it follows that ν_1 is inactive; ν_2 is active and the radiation is polarized in a plane perpendicular to the axis; and ν_3 is also active but the radiation is polarized along the axis of the molecule. In general, in a molecule possessing a center of symmetry, vibrations that are symmetrical with respect to the symmetry axis are inactive in absorption, while vibrations that are antisymmetrical with respect to the center are active.

As another example, let us take the symmetrical triangular YX_2 molecule of which the water molecule is an example. Let a set of coordinate axes be chosen with the origin at the center of gravity of the molecule, the z axis along the symmetry axis and the y and x axes perpendicular to the plane and in the plane of the molecule respectively (Fig. 8). It follows from Fig. 2 and the discussions on the forms of the three normal vibrations in §3 that

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[5] When one is dealing with a large number of molecules in the gaseous or vapor state, the polarization character of the radiation of course will not show up in absorption experiments on account of the random orientations of the molecules. In crystals, however, in which the ions or groups of atoms are lined up, it is possible to distinguish between the various directions of the electric moment relative to the symmetry elements of the crystal. See Chap. V on the carbonates and chlorates.

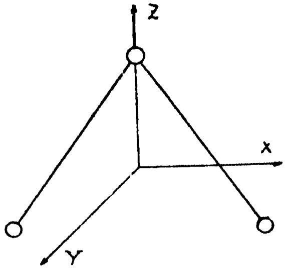

Fig. 8

$$\left(\frac{\partial\mathfrak{M}_z}{\partial X_1}\right)_0 \neq 0, \qquad \left(\frac{\partial\mathfrak{M}_z}{\partial X_2}\right)_0 \neq 0, \qquad \left(\frac{\partial\mathfrak{M}_z}{\partial X_3}\right)_0 = 0,$$
$$\left(\frac{\partial\mathfrak{M}_x}{\partial X_1}\right)_0 = 0, \qquad \left(\frac{\partial\mathfrak{M}_x}{\partial X_2}\right)_0 = 0, \qquad \left(\frac{\partial\mathfrak{M}_x}{\partial X_3}\right)_0 \neq 0,$$
$$\left(\frac{\partial\mathfrak{M}_y}{\partial X_1}\right)_0 = \left(\frac{\partial\mathfrak{M}_y}{\partial X_2}\right)_0 = \left(\frac{\partial\mathfrak{M}_y}{\partial X_3}\right) = 0. \tag{49}$$

Hence all the three fundamental vibrations are active. In ν_1 and ν_2, the change of the electric moment is along the symmetry axis while in ν_3 it is perpendicular to the symmetry axis of the molecule. We shall show in Chap. IV that these two types of vibrations give rise to two different types of structure in the vibration-rotational bands in the absorption spectrum.

On entirely similar considerations, the selection rules for the different molecular models discussed in Chap. V can be obtained.

Finally let us consider the selection rules for the harmonics of the fundamental vibrations of a molecule. For this purpose we have to consider the deviation of the vibrations from pure simple harmonics motions, and consequently instead of (10) we have to express the coordinates X's by the general Fourier series (38). In a molecule completely devoid of symmetry, all harmonics of the fundamentals may be expected to be active, although the higher harmonics may be very weak since their intensities depend on the coefficients A_{im} in the Fourier series, which in turn depend on the effect of the anharmonicities of the vibrations. If in a vibration ν_i the molecule remains symmetrical with respect to a center of symmetry, then the vibration and all its harmonics will be inactive. If in the vibration ν_i the molecule is antisymmetrical with respect to the center of symmetry, then the electric moment $\mathfrak{M}_x$, say, must go to its negative after half a period of ν_i, *i.e.*, $\mathfrak{M}_x(t) = -\mathfrak{M}_x\left(t + \frac{1}{2\nu_i}\right)$. This requires that all the coefficients of terms in $2\nu_i$, $4\nu_i$, $6\nu_i$ ······ etc. must vanish. Consequently only the harmonics $3\nu_i$, $5\nu_i$ $7\nu_i$ ······· etc. will be active. The same results are obtained in the wave-mechanical treatment, as will be shown in Chap. III, §3.

We shall now come to the selection rules in the Raman effect. It has been shown in §5 that the induced electric moments and hence the intensities of the scattered radiations are determined by the quantities $\left(\frac{\partial\alpha_{xx}}{\partial X_i}\right)_0$, $\left(\frac{\partial\alpha_{yy}}{\partial X_i}\right)_0$, . . . $\left(\frac{\partial\alpha_{zx}}{\partial X_i}\right)_0$. The vanishing of some of the coefficients will give rise to scattered radiations of a definite polarization character, while the vanishing of all these coefficients will give a zero intensity to the Raman line in question. The quantitative calculation of these quantities for a given molecule necessitates a knowledge of the electronic structure of the molecule, which is at present still meagre for all but the simplest of diatomic molecules. Important and useful informations, however, such as the selection and the polarization rules, can be obtained simply from considerations of the symmetry properties of the molecule and its vibrations alone. In the following we shall only discuss a few molecular models as illustrations, but give the results for other molecular models in Chap. V. For further details, the reader must be referred to the works of Placzek and others.[6]

Let us take again the linear symmetrical YX_2 molecule and choose the axis of the molecule as the z-axis, and two perpendicular axes as the x and the y axes, the origin being at the center of the molecule. The polarizability tensor α is then an ellipsoid of revolution, with its principal axes along the coordinate axes. Hence the components $(\alpha_{xy})^0 = (\alpha_{yz})^0 = (\alpha_{zx})^0 = 0$. During the normal vibrations ν_1, ν_2 and ν_3, Fig. 3, the directions of the principal axes of the polarizability ellipsoid obviously remain unchanged. Hence one has

$$\left(\frac{\partial\alpha_{xy}}{\partial X_i}\right)_0=\left(\frac{\partial\alpha_{yz}}{\partial X_i}\right)_0=\left(\frac{\partial\alpha_{zx}}{\partial X_i}\right)_0=0. \qquad (50)$$

It is evident that the components α_{xx}, α_{yy}, α_{zz} do not change during the vibrations ν_2 and ν_3, but they do change during the vibration ν_1, *i.e.*,

$$\left(\frac{\partial\alpha_{xx}}{\partial X_1}\right)_0=\left(\frac{\partial\alpha_{yy}}{\partial X_1}\right)_0\neq 0, \qquad \left(\frac{\partial\alpha_{zz}}{\partial X_1}\right)_0\neq 0,$$

$$\left(\frac{\partial\alpha_{xx}}{\partial X_2}\right)_0=\left(\frac{\partial\alpha_{yy}}{\partial X_2}\right)_0=\cdots\cdots\left(\frac{\partial\alpha_{zz}}{\partial X_3}\right)_0=0. \qquad (51)$$

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[6] C. Placzek, *Leipziger Vorträger* (1931); *Handbuch der Radiologie*, **Bd 6/II**, (1934); H. A. Stuart, *Molekülstruktur*, (1934).

Hence only ν_1 is active in the Raman effect.

On the other hand, if one considers a linear unsymmetrical X-Y-Z molecule, then while equations (50) still hold for the vibrations ν_1 and ν_3, they no longer hold for the vibration ν_2. From Fig. 9, it can be seen that the directions of the principal axes of the polarizability ellipsoid no longer remain unchanged in the vibration ν_2. Hence one has

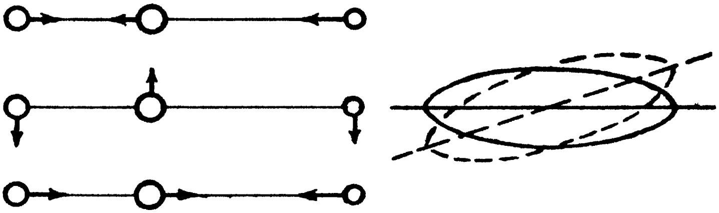

Fig. 9

$$\left(\frac{\partial \alpha_{xy}}{\partial X_2}\right)_0 \neq 0, \quad \left(\frac{\partial \alpha_{yz}}{\partial X_2}\right)_0 = \left(\frac{\partial \alpha_{zx}}{\partial X_2}\right)_0 \neq 0. \tag{52}$$

Also, instead of (51), we now have

$$\left(\frac{\partial \alpha_{xx}}{\partial X_1}\right)_0 \neq 0, \cdots\cdots\cdots\cdots \left(\frac{\partial \alpha_{zz}}{\partial X_3}\right)_0 \neq 0. \tag{53}$$

That is, all the three normal vibrations of the molecule X-Y-Z are active in the Raman effect.

To obtain the state of polarization of the scattered radiation, it is necessary to determine the relative values of the components of the electric moment in different directions. Experimentally one usually measures the ratio of the intensities of the scattered radiations with the electric vector perpendicular to that of the exciting radiation and those with the electric vector parallel to that of the exciting radiation.[7] This ratio is defined as the degree of depolarization ϱ. Since the intensity of the scattered radiations is proportional to the square of the induced electric moment, the degree of depolarization can be obtained by taking the ratio of the squares of the components of the induced electric moment averaged over all the possible orientations of the molecule with respect to the direction of the electric vector of the exciting radiation. Thus the degree of depolarization is a measure of the anisotropy of the change of the polarizability tensor due to the vibration of the molecule. If in particular the vibration of a molecule is spherically symmetrical, then the tensor whose components are $\left(\frac{\partial\alpha_{xx}}{\partial X_i}\right)_0 X_i, \left(\frac{\partial\alpha_{yy}}{\partial X_i}\right)_0 X_i \cdots\cdots\cdots\cdots$ becomes a sphere and the degree of depolarization is accordingly zero. We shall not go into the detailed calculation of ϱ for a molecule in general. Suffice it to say that in general the value of ϱ lies between O and 6/7 when ordinary (unpolarized) radiation is used for exciting the Raman line, and between O and 3/4 when linearly polarized radiation is used for excitation. Vibrations that are symmetrical with respect to some elements of symmetry but antisymmetrical with respect to another element of symmetry have the value $\varrho=6/7$ (or 3/4 with polarized radiation for excitation); while vibrations that are symmetrical with respect to all elements of symmetry usually have very low values of ϱ. Their exact values, however, depend on the structure of the molecule in question and cannot be given in general.

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[7] W. Hanle, Naturwiss. 19, 375, (1931); Phys. Zeits. 32, 556, (1931); Ann. der Physik 11, 885, (1931); 15, 345, (1932), and also R. Bär, Naturwiss. 19, 463, (1931); Helv. Phys. Acta 4, 131, (1931), developed the method of using circularly polarized radiation for exciting the Raman lines. It was found that the scattered radiation (Raman scattering) consists of circularly polarized radiations both in the same sense of rotation as the exciting radiation and in the reversed sense. The ratio of the intensity of the reversed or "umgekehrt" polarized radiation to that of the "richtig" polarized radiation is defined as the reversion coefficient *P*. A detailed analysis shows that the coefficient *P* is related to the degree of depolarization ρ with linearly polarized exciting radiation through the equation $P=2\rho/(1-\rho)$. It is seen that highly symmetrical vibrations (low values of ρ) show low values of *P*, and completely depolarized radiation ($\rho=3/4$) have the high value 6 for *P*. Thus from measurements of *P*, it is also possible to obtain informations concerning the symmetry of the vibrations of a molecule.

§7. Isotope Effect

When an atom (or a few atoms) in a molecule is replaced by an isotope, it is reasonable to assume that the potential field of the molecule is unchanged since it is determined by the electronic structure of the molecule alone. The difference in the masses of the isotopes, however, will (*i*) bring about a change in the frequencies of the normal vibrations of the molecule, and (*ii*) lower the symmetry of the molecule, thereby removing the degeneracy of certain vibrations and causing certain inactive vibrations to become active, if such vibrations are present in the original molecule. Theoretically, the isotope shifts in the frequencies of the normal vibrations can be calculated in terms of the masses of the atoms and the constants in the potential function by the method of §1. Such calculations are, however, usually quite complicated, except for a few molecular models. As illustrations, we shall only give the results for the symmetrical YX_2 molecule according to (*i*) the valence force treatment, and (*ii*) the general force treatment.

(1) Valence force treatment[1]

When one of the X atoms of mass m is replaced by an isotope of mass $m+\Delta m$, the following results are obtained from equs. (22)

$$\Delta\lambda_1 + \Delta\lambda_2 = -(k + 2k_\alpha)\frac{\Delta m}{2m^2},$$

$$\lambda_1\Delta\lambda_2 + \lambda_2\Delta_1 = -\frac{4k\,k_\alpha}{\mu}\cdot\frac{\Delta m}{2m^2},$$

$$\Delta\lambda_3 = -k\frac{\Delta m}{2m^2}\;;\;\text{or}\;\frac{\Delta\lambda_3}{\lambda_3} = -\frac{M}{M+m(1-\cos\alpha)}\,\frac{\Delta m}{2m}. \tag{55}$$

In the particular case of a linear symmetrical molecule, there result from equations (24) the following expressions

$$\Delta\lambda_1 = \Delta\lambda_3 = -k\frac{\Delta m}{2m^2},$$

$$\Delta\lambda_2 = -2k_\alpha\frac{\Delta m}{2m^2}\;;\;\text{or}\;\frac{\Delta\lambda_2}{\lambda_2} = -\frac{M}{M+2m}\cdot\frac{\Delta m}{2m}. \tag{56}$$

In this case, the vibration ν_1 is no longer symmetrical with respect to the center and hence becomes active in absorption.

When the Y atom of mass M is replaced by an isotope of mass $M+\Delta M$, equations (22) give for the triangular molecule the relations

$$\Delta\lambda_1 + \Delta\lambda_2 = -\left[k(1+\cos\alpha) + 2k_\alpha(1-\cos\alpha)\right]\frac{\Delta M}{M^2},$$

$$\lambda_1\Delta\lambda_2 + \lambda_2\Delta\lambda_1 = -\frac{4k\,k_\alpha}{m}\cdot\frac{\Delta M}{M^2}, \tag{57}$$

$$\Delta\lambda_3 = -k(1-\cos\alpha)\frac{\Delta M}{M^2}\;;\;\text{or}\;\frac{\Delta\lambda_3}{\lambda_3} = -\frac{m(1-\cos\alpha)}{M+m(1-\cos\alpha)}\cdot\frac{\Delta M}{M},$$

which reduce, in the case of a linear molecule, to

$$\Delta\lambda_1 = 0,$$

$$\Delta\lambda_2 = -4k_\alpha\frac{\Delta M}{M^2}\;;\;\Delta\lambda_3 = -2k\frac{\Delta M}{M^2} \tag{58}$$

or

$$\frac{\Delta\lambda_2}{\lambda_2} = \frac{\Delta\lambda_3}{\lambda_3} = -\frac{2m}{M+2m}\cdot\frac{\Delta M}{M}.$$

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[1] Expressions for the isotope shifts for the general triatomic molecule according to the valence force treatment have been given by Adel, Phys. Rev. 45, 56, (1934). It is to be noted that the A, B, C in his expressions for the linear molecule have different meanings, namely, $A=\lambda_1+\lambda_2$, $B=\lambda_1\lambda_2$, and $C=\lambda_3$, from those for the general case. Equations (55)—(58) here can be obtained as special cases of his general expressions.

In these two cases, the symmetry of the molecule is not disturbed. Hence the selection rules are unaffected.

All the above expressions (55)—(58) are approximate only and can not be used if $\Delta m/m$ or $\Delta M/M$ is much greater than 1/10. If both of the X atoms are replaced by the isotope of mass $m+\Delta m$, then the frequency shifts are given, to the same approximation as before, by (55) and (56) in which Δm is replaced by $2\Delta m$.[2] In this case, the symmetry of the molecule and hence the selection rules remain unaffected.

(2) General force treatment

In this case, corresponding to the equations (55)—(58) in the valence force treatment, one obtains from equations (27) the following sets of relations

Triangular[3]

$$\left.\begin{aligned} &X^{m}Y^{M}X^{m+\Delta m} && \Delta\lambda_1+\Delta\lambda_2=-\left(2A+\frac{C}{2}\right)\frac{\Delta m}{2m^2}\,,\\ & && \frac{\Delta\lambda_1}{\lambda_1}+\frac{\Delta\lambda_2}{\lambda_2}=-\frac{M+m}{M+2m}\cdot\frac{\Delta m}{2m}\,,\\ &\text{or} && \frac{\lambda_1^*}{\lambda_1}\frac{\lambda_2^*}{\lambda_2}=1-\frac{M+m}{M+2m}\cdot\frac{\Delta m}{m}\,,\\ & && \frac{\Delta\lambda_3}{\lambda_3}=-p\left[1-\frac{2\,mp\cot^2\alpha}{M\,(1+p\cot^2\alpha)}\right]\frac{\Delta m}{2m}\,, \end{aligned}\right\}\quad(59)$$

Linear

$$\left.\begin{aligned} &X^{m}Y^{M}X^{m+\Delta m} && \frac{\Delta\lambda_1}{\lambda_1}=-\frac{\Delta m}{2m}\,,\\ & && \frac{\Delta\lambda_2}{\lambda_2}=\frac{\Delta\lambda_3}{\lambda_3}=-p\frac{\Delta m}{2m}\,,\\ &\text{or} && \frac{\lambda_1^*}{\lambda_1}\frac{\lambda_3^*}{\lambda_3}=1-\frac{M+m}{M+2m}\cdot\frac{\Delta m}{m}\,. \end{aligned}\right\}\quad(60)$$

Triangular

$$\left.\begin{aligned} &X^{m}Y^{M+\Delta M}X^{m} && \Delta\lambda_1+\Delta\lambda_2=-C\frac{\Delta M}{M^2}\,,\\ & && \frac{\Delta\lambda_1}{\lambda_1}+\frac{\Delta\lambda_2}{\lambda_2}=-2mp\frac{\Delta M}{M^2}\,,\\ & && \frac{\Delta\lambda_3}{\lambda_3}=-2mp\left(\frac{1+2p\cot^2\alpha}{1+p\cot^2\alpha}\right)\frac{\Delta M}{M^2}\,. \end{aligned}\right\}\quad(61)$$

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[2] See Teller, *Hand-und Jahrbuch der chemischen Physik*, Bd 9/II, Pp. 141 ff.

[3] The expressions for $\Delta\lambda_3$ given by Rosenthal, Phys. Rev. 42, 813, (1932); 45, 426, (1934), are in error because of an error in the expression for λ_3. See footnote (1) in §3, C.

Linear

$$X^{m}Y^{M+\Delta M}X^{m} \qquad \left.\begin{aligned} \Delta\lambda_1 &= 0, \\ \frac{\Delta\lambda_2}{\lambda_2} = \frac{\Delta\lambda_3}{\lambda_3} &= -2m\mu\frac{\Delta M}{M^2} \end{aligned}\right\} \tag{62}$$

The same remarks given for the valence force treatment also apply here. It is seen from (59) and (61) that the observation of the isotope shift in ν_3 enables the apex angle 2α to be determined if it is not known from other data; and the isotope shifts in ν_1 and ν_2 due to the replacement of the Y atom enable the constant C in the potential function (26) to be determined. The other constants A, B, D can then be obtained from equations (27).

Calculations of the isotope shifts in other molecules such as YX_3, YX_4 have been carried out by Rosenthal.[4] The results are more complicated than those in the case of the YX_2 molecule. We shall refer to her papers for these cases but shall give another perturbation method for the calculation of isotope shifts, which is due to Rayleigh and is suggested for this purpose by Wilson.[5]

Let the displacements of an atom i of mass m_i in a molecule be described by a set of rectangular coordinates q''s with origin at the position of equilibrium of m_i, and let us define the generalized coordinates

$$q_i = \sqrt{m_i}\, q'_i . \tag{63}$$

The kinetic energy is then $T = \frac{1}{2}\sum_i \dot{q}_i^2$. Let the potential energy be

$$2V = \Sigma\, b_{ij}\, q_i\, q_j , \tag{64}$$

and let the transformation that reduces V and T simultaneously to the normal forms be given by

$$Q_k = \Sigma\, c_{ik}\, q_i . \tag{65}$$

As the coefficients b_{ij} in (64) are functions of the potential constants and the m_i's, the replacement of some of the atoms by their isotopes will change the potential energy V into V',

$$2V' = \Sigma\, b'_{ij}\, q_i\, q_j . \tag{66}$$

Let us regard the difference

$$2V_1 = 2\,(V' - V) = \Sigma\, B_{ij}\, q_i\, q_j \tag{67}$$

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[4] J. E. Rosenthal, Phys. Rev. 45, 436, (1934); 47, 235, (1935) for YX_3; Phys. Rev. 45, 538, 766; 46, 730, (1934) for YX_4.

[5] E. B. Wilson, jr. Phys. Rev. 45, 427, (1934).

as a perturbation. The transformation (65) applied to V_1 will not give a normal form, but in a first approximation, we may neglect the cross terms and consider only the square terms

$$2V_1 = \Sigma \Delta\lambda_i Q_i^2 ,$$

where

$$\Delta\lambda_k = \sum_{i,j} c_{ik} B_{ij} c_{jk} , \tag{68}$$

or, if the matrix of the transformation (65) be denoted by C,

$$\Delta\lambda_k = (C^{-1} B C)_{kk} . \tag{68a}$$

If in a molecule two vibrations Q_k and Q_r have the same frequency, the effect of the isotope replacement is to remove the degeneracy by giving two distinct (in general) shifts by the equation

$$\begin{vmatrix} (C^{-1} B C)_{kk} - \Delta\lambda & (C^{-1} B C)_{kr} \\ (C^{-1} B C)_{rk} & (C^{-1} B C)_{rr} - \Delta\lambda \end{vmatrix} = 0, \tag{69}$$

where

$$(C^{-1} B C)_{kr} = \sum_{i,j} c_{ik} B_{ij} c_{jk} . \tag{70}$$

As an illustration of this method, let us calculate again the isotope shift of the inactive frequency ν_1 of the linear symmetrical YX_2 molecule when one of the X atoms of mass m is replaced by an isotope of mass $m+\Delta m$, and let $X_1 = \sqrt{m}\, x_1$, $X_2 = \sqrt{m}\, x_2$ where x_1 and x_2 are the displacements of the two X atoms. The introduction of the normal coordinate $Q = \frac{1}{\sqrt{2}}(X_1 - X_2)$ reduces the kinetic and the potential energies to the normal forms $2T = \dot{Q}^2$, $2V = \left(\frac{2A}{m}\right) Q^2$, where A is defined in (26). Then one obtains

$$2V_1 = A\left[\left(\frac{1}{m+\Delta m} - \frac{1}{m}\right) X_1^2 - \frac{2}{\sqrt{m}}\left(\frac{1}{\sqrt{m+\Delta m}} - \frac{1}{\sqrt{m}}\right) X_1 X_2 \right].$$

As $c_{11} = - c_{21} = \frac{1}{\sqrt{2}}$, (68) gives

$$\frac{\Delta\lambda}{\lambda} = -\frac{\Delta m}{2m}$$

in agreement with (60).

In systems like this, it is of course possible to obtain the isotope shifts by more direct methods (for example, the above result can be obtained simply from the relation $\lambda = 2A/m$). But in other more complicated molecules, this method may prove useful. Further illustrations are given by Wilson for the single inactive frequency of the tetrahedral YX_4 molecule.

CHAPTER III

VIBRATIONS OF MOLECULES: THE QUANTUM THEORY

In the last chapter, we have presented the classical theory of the vibrational spectra of molecules. From the classical treatment, one obtains the relations between the frequencies of the normal vibrations and the constants in the potential function of a molecule, the forms of the individual vibrations, the selection rules in the absorption and the Raman spectra, and the isotope shifts. When one considers, however, such questions as the effect of the anharmonicities on the energy of vibrations, the detailed structure of the vibration-rotational bands, and the phenomena of resonance between two or more energy levels, the quantum theory proves to be more adequate. In this chapter, we shall present the quantum theory aspects of the problem of the vibrations of molecules.

§1. Harmonic and Anharmonic Vibrators

Just as the simple harmonic oscillator forms the basis for the discussion of the vibrations of molecules in the classical theory, so it also forms a convenient initial approximation for the treatment of the vibrations of molecules in the quantum theory. The theory of the harmonic and anharmonic oscillators according to the wave mechanics is well known. But for convenience in our later discussions, we shall give the important results below.

A) Wave mechanics of the harmonic oscillator

The Schroedinger equation of a harmonic oscillator of mass μ and fundamental frequency ν is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}(E - 2\pi^2\nu^2\mu x^2)\psi = 0. \tag{1}$$

The eigenvalues of (1), which give the energies of the oscillator, are given by[1]

$$E_v = (v + \tfrac{1}{2})h\nu, \qquad v = 0, 1, 2 \cdots\cdots. \tag{2}$$

The eigenfunctions are

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[1] See any text on the wave mechanics, for example, Sommerfeld's *Wave Mechanics.*

$$\psi_v(\xi) = e^{-\frac{\xi^2}{2}} H_v(\xi), \tag{3}$$

where

$$\xi = \sqrt{\alpha}\, x, \qquad \alpha = \frac{4\pi^2 \mu \nu}{h}. \tag{4}$$

$H_n(\xi)$ is the Hermitian polynomial of degree n and is given by

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n} \tag{5}$$

or explicitly

$$H_n(\xi) = (2\xi)^n - \frac{n(n-1)}{1}(2\xi)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2\,!}(2\xi)^{n-4}$$

$$+ \cdots\cdots + \begin{cases} (-1)^{\frac{n}{2}} \dfrac{n!}{(\frac{n}{2})!}, & \text{for } n \text{ even}, \\ (-1)^{\frac{n-1}{2}} \dfrac{n!}{(\frac{n-1}{2})!}(2\xi), & \text{for } n \text{ odd}. \end{cases} \tag{6n}$$

It satisfies the recurrence formula

$$H_{n+1}(\xi) - 2\xi H_n(\xi) + 2n H_{n-1}(\xi) = 0. \tag{6}$$

The properties of these eigenfunctions ψ_n in (3) are as follows:

a)
$$\psi_n(\xi) = \psi_n(-\xi), \qquad \text{for } n \text{ even},$$
$$\psi_n(\xi) = -\psi_n(-\xi), \qquad \text{for } n \text{ odd}; \tag{7}$$

b)
$$\int_{-\infty}^{\infty} \overset{*}{\psi}_m \psi_n \, d\xi = \begin{cases} 0, & m \neq n, \\ 2^n\, n!\, \sqrt{\pi}, & m = n; \end{cases} \tag{8}$$

that is, the eigenfunctions are even or odd in the argument according as n is even or odd, and that the eigenfunctions form an orthogonal set. We shall normalize the ψ by the relation

$$\int_{-\infty}^{\infty} \overset{*}{\psi}_n(x)\, \psi_n(x)\, dx = 1. \tag{9}$$

Because of the substitution (4), the normalized eigenfunction for the state n is

$$\Psi_n(\xi) = \frac{\sqrt[4]{\alpha}}{\sqrt{2^n\, n!\, \sqrt{\pi}}} e^{-\frac{\xi^2}{2}} H_n(\xi), \tag{10}$$

The selection rule for the harmonic oscillator can be obtained. Since the process of emission or absorption of radiation is governed by the change of the electric moment of the system, the question whether a transition between a state m and a state n is observed in emission or absorption can be answered by an examination of the matrix element of the electric moment associated with the two states m and n, or, since the electric moment is proportional to the displacement x, by an examination of the matrix element $(x)_{mn}$,

$$(x)_{mn} = \int_{-\infty}^{\infty} \overset{*}{\psi}_m \, x \, \psi_n \, dx. \tag{11}$$

It can easily be shown by means of (6) that $(x)_{mn}$ vanishes except for $m = n \pm 1$; and

$$(x)_{n,n+1} = (x)_{n+1,n} = \sqrt{\frac{h\,(n+1)}{8\,\pi^2 \mu \nu}}. \tag{12}$$

Hence it follows that the selection rule is

$$\Delta n = \pm\, 1, \tag{13}$$

that is, in the spectrum of a harmonic oscillator, only the fundamental frequency ν is emitted or absorbed. This is in agreement with the classical theory.

B) Anharmonic oscillator

(i) Perturbation treatment

The application of the theory of a harmonic oscillator to the problem of the vibrations of a diatomic molecule constitutes what may be called a zeroth approximation. The potential functions in the actual molecules are usually such that they increase more rapidly than the quadratic function $\frac{1}{2}kx^2$ when the two atoms are compressed together, but less rapidly than $\frac{1}{2}kx^2$ when the two atoms are stretched apart from the position of equilibrium. One way to take into account the deviation from the harmonic motion is to include the higher order terms in the Taylor expansion of the potential energy (equ. (3) of Chap. II). Let us now take for the energy of the oscillator the expression

$$V = \tfrac{1}{2}\, k_1\, x^2 + \tfrac{1}{6}\, k_2\, x^3 + \frac{1}{24}\, k_3 x^4. \tag{14}$$

The problem then is to find *i*) the change in the energy of the state n due to the introduction of the terms in k_2 and k_3, and *ii*) the selection rule for this anharmonic oscillator.

To find the energy of the oscillator with the potential (14), it would be necessary to find the eigenvalues of the Schroedinger equation with this potential. When k_2 and k_3 are small compared with k_1, an approximate solution can be obtained by the method of the perturbation theory. If the perturbing potential is expressed in the form $\lambda V_1 + \lambda^2 V_2$ where λ is simply a parameter to remind one of the order of smallness, then according to the perturbation theory, the change in energy up to the first power of λ is

$$\lambda E'_n = \lambda \int_{-\infty}^{\infty} \overset{*}{\Psi}_n V_1 \Psi_n \, dx, \tag{15}$$

and the energy change up to the second power of λ is

$$\lambda^2 E''_n = \lambda^2 \int_{-\infty}^{\infty} \overset{*}{\Psi}_n V_2 \Psi_n \, dx + \lambda^2 \Sigma' \frac{\left[\int_{-\infty}^{\infty} \overset{*}{\Psi}_n V_1 \Psi_i \, dx\right]^2}{E^{\circ}_n - E^{\circ}_i}, \tag{16}$$

where $E^{\circ}_n = (n+½)h\nu$ and is the zeroth order energy corresponding to the potential $V_0 = ½ k_1 x^2$, and the summation is taken over all states i different from n.

Applying these general results to (14) and assuming that $k_2 \gg k_3$, one obtains for the first order energy change

$$E'_n = 0, \tag{17}$$

and for the second order energy change

$$E''_n = \frac{h^2 k_3 \nu}{32 \pi \sqrt{\mu}\, k_1^3} (n^2 + n + \tfrac{1}{2}) - \frac{5 h^2 \nu k_2^2}{96 \pi \sqrt{\mu} k_1^6} (n^2 + n + \frac{11}{30}). \tag{18}$$

The sign of k_2 is always negative, corresponding to the behavior of the potential function described at the beginning of this section. In most molecules it is usually such that the second term in (18) is greater than the first. Thus the anharmonic terms in the potential (14) bring about a negative correction to the zeroth order energy, which is proportional to the square of the quantum number n, in agreement with the empirical results of the analyses of band spectra of molecules.[1]

The calculation of the energy changes in (18) involves the evaluation of integrals of the type

$$\int_{-\infty}^{\infty} e^{-x^2} x^p H_n(x) H_m(x) \, dx.$$

Such integrals can be evaluated either by repeated applications of the recurrence formula (6), or by expanding $x^p H_n(x)$, if $n<m$, into a series of $H_i(x)$

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[1] The empirical results of band spectrum analyses prefer an energy expression of the form $E = h\nu (n+½) - xh\nu (n+½)^2$. See (ii) of this section below, equ. (31a).

$$x^p H_n(x) = \sum_i^{n+p} c_i H_i(x), \tag{19}$$

the summation beginning with 0 or 1 according as $n+p$ is even or odd. Because of the property (7), it follows that if $n+p$ is even (or odd), all the odd (or even) coefficients c_i vanish. The non-vanishing c_i's may be easily determined by comparing the coefficients of each power of x on both sides of equation (19). We give below a few of such integrals which are of frequent occurrence in the perturbation calculations of the vibrational energies of molecules.

$$\begin{aligned}
\int_{-\infty}^{\infty} \overset{*}{\Psi}_n\, x\, \Psi_{n+1}\, dx &= \sqrt{\frac{n+1}{2}},\\
\int_{-\infty}^{\infty} \overset{*}{\Psi}_n\, x^2\, \Psi_n\, dx &= \frac{2n+1}{2},\\
\int_{-\infty}^{\infty} \overset{*}{\Psi}_n\, x^2\, \Psi_{n+2}\, dx &= \tfrac{1}{2}\sqrt{(n+1)(n+2)},\\
\int_{-\infty}^{\infty} \overset{*}{\Psi}_n\, x^3\, \Psi_{n+1}\, dx &= 3\left(\frac{n+1}{2}\right)^{\frac{3}{2}},\\
\int_{-\infty}^{\infty} \overset{*}{\Psi}_n\, x^3\, \Psi_{n+3}\, dx &= \sqrt{\frac{(n+1)(n+2)(n+3)}{8}},\\
\int_{-\infty}^{\infty} \overset{*}{\Psi}_n\, x^4\, \Psi_n\, dx &= \tfrac{3}{2}\left(n^2+n+\tfrac{1}{2}\right).
\end{aligned} \tag{20}$$

To obtain the selection rule for the anharmonic oscillator, it is necessary to examine the matrix element of $\mathfrak{M}_x \propto x$ with respect to the eigenfunctions of the anharmonic oscillator, *i.e.*, of the perturbed system. According to the perturbation theory, if the eigenfunctions of the unperturbed system be denoted by ψ_n°, the first order change in the eigenfunction of the state n due to the perturbing potential λV_1 is

$$\lambda \psi'_n = \lambda \sum_i{}' a_i^n \psi_i^\circ = \lambda \sum_i{}' \frac{\int_{-\infty}^{\infty} \overset{*}{\Psi}{}_n^\circ V_1 \Psi_i\, dx}{E_n^\circ - E_i^\circ} \psi_i^\circ, \tag{21}$$

where the summation is taken over all states $i \neq n$. Consider first the effect of the perturbing potential $\frac{1}{6} k_2 x^3$. Then the eigenfunction of the state n up to the first power of λ is[2]

$$\Psi_n = \Psi^{\circ}_n + \lambda \Psi'_n = \Psi^{\circ}_n + \lambda \Big[a^n_{n+1} \psi^{\circ}_{n+1} + a^n_{n-1} \psi^{\circ}_{n-1} + a^n_{n+3} \psi^{\circ}_{n+3} + a^n_{n-3} \psi^{\circ}_{n-3} \Big] \tag{22}$$

Substitution of this and a similar expression for $\Psi^{\circ}_m + \lambda \Psi'_m$ into the integral for the matrix element of x, namely (11), gives

$$(x)_{mn} = \int_{-\infty}^{\infty} (\overset{*}{\Psi}{}^{\circ}_m + \lambda \overset{*}{\Psi}{}'_m)\, x\, (\Psi^{\circ}_n + \lambda \Psi'_n)\, dx. \tag{23}$$

From (23) it follows that up to the zeroth power in λ, $(x)_{mn}$ does not vanish for $m = n \pm 1$, and up to the first power in λ, $(x)_{mn}$ does not vanish for $m = n$, $n \pm 2$, $n \pm 4$. Similarly if the perturbation $\frac{1}{24} k_3 x^4$ is considered, then up to the first power in λ, $(x)_{mn}$ will not vanish for $m = n \pm 3$, $n \pm 5$. Hence for the anharmonic oscillator (14), the selection rule is

$$\Delta n = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5. \tag{24}$$

This shows that in the spectrum, in addition to the fundamental frequency ($\Delta n = \pm 1$), harmonics up to the fourth ($\Delta n = \pm 2, 3, 4, 5$) are also present. By including higher order terms in the potential, still higher harmonics can be accounted for in a similar manner. Since the intensities of these harmonics are determined by the coefficients a^n_i's and hence by the coefficients k's of the anharmonic terms in the potential, it is seen why the harmonics are usually weak and the intensity decreases as Δn increases.

(ii) Morse oscillator

For a number of diatomic molecules, the potential function

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[2] It is seen from (22) that as the result of the perturbation V_1, the state n is no longer described by ψ°_n alone but by a wave function containing the contributions of other states. When the a^n_i's are small and hence the contributions from the other states are small, one may still speak of the state n. When the non-diagonal elements of V_1 are quite large and hence the a^n_i's, each state is described by a combination of the wave functions of a number of states and it is no longer justified to refer to any state by the quantum number n which has an exact meaning only in the unperturbed system. In fact, in such cases, the perturbation theory for degenerate systems must be used instead of (21) above. See Pp. 83-89.

$$V = D(1-y)^2, \qquad y = e^{-a(r-r_0)} \tag{25}$$

suggested by Morse[1] has been found very successful. In (25), r_0 is the equilibrium separation of the molecule, a is a parameter to be determined from the empirical data for each individual molecule, and D is another parameter giving the energy of dissociation of the molecule also to be determined from the empirical data. The general form of the potential curve is shown in Fig. 10.

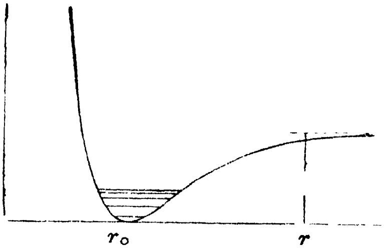

Fig. 10. Morse potential curve

The Schroedinger equation of an oscillator with this potential can be written, after transforming to the independent variable y, in the form

$$\frac{1}{y}\,\frac{d}{dy}\left(y\,\frac{d\psi}{dy}\right)+\frac{8\pi^2\mu}{a^2h^2}\left[\frac{E-D}{y^2}+\frac{2D}{y}-D\right]\psi = 0. \tag{26}$$

On assuming

$$\psi = e^{-\frac{z}{2}}z^{\frac{\beta}{2}}F(z), \tag{27}$$

where

$$z = 2\alpha y, \qquad \alpha = \frac{2\pi\sqrt{2\mu D}}{a\,h}. \qquad E-D = -\frac{a^2h^2\beta^2}{32\pi^2\mu}, \tag{28}$$

one obtains the following differential equation for F(z)

$$zF'' + (\beta+1-z)F' + \tfrac{1}{2}(2\alpha-\beta-1)F = 0. \tag{29}$$

On assuming the series solution

$$F(z) = \Sigma\, c_k z^k \tag{30}$$

and requiring the series to stop at $k=n$, one obtains the eigenvalues of (29), namely,

$$2n - 2\alpha + \beta + 1 = 0, \tag{31}$$

or, from (28),

$$E_n = (n+\tfrac{1}{2})h\nu - x(n+\tfrac{1}{2})^2h\nu, \tag{31a}$$

where

$$\nu = \frac{a}{2\pi}\sqrt{\frac{2D}{\mu}} \tag{32}$$

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[1] P. M. Morse, Phys. Rev. 34, 57, (1929); see also N. Rosen, Jour. Chem. Phys. 1, 319, (1933) for the asymptotic solutions of (26).

is the frequency of infinitesmal vibration of the oscillator (that is, of an oscillator whose potential is obtained by expanding y in (25) and neglecting all terms of higher powers than the second in $(r-r_0)$. In (31a), the coefficient x is given by

$$x = \frac{1}{2\alpha} = \frac{h\nu}{4D} = \frac{ha^2}{8\pi^2\mu\nu}. \tag{33}$$

With the relation (31), one can show that the recurrence formula for the coefficients c_k in (30) is

$$c_{k+1} = \frac{k-n}{(k+1)(k+\beta+1)} c_k. \tag{34}$$

By means of the gamma function

$$\Gamma(t) = \int_0^\infty e^{-z} z^{t-1} dz \tag{35}$$

and the reduction formula

$$\Gamma(t+1) = t\,\Gamma(t), \tag{36}$$

the normalizing factor for the function $\psi(z)$ in[2]

$$N_n^2 \int_{-\infty}^{\infty} \Big[\psi_n(z)\Big]^2 dr = \frac{1}{a} N_n^2 \int_0^\infty \Big[\psi_n(z)\Big]^2 \frac{dz}{z} = 1 \tag{37}$$

can be found to be

$$\begin{aligned} N_n^2 &= \frac{a(1-x)(1-2x)\cdots(1-nx)[1-(n+1)x]^2\cdots(1-2nx)^2[(1-(2n+1)x]}{n!\,x^{3n+1}\Gamma\left(\frac{1}{x}\right)} \\ &= \frac{a[1-(n+1)x]\cdots\cdots(1-2nx)}{n!\,x^n\,\Gamma\left(\frac{1}{x}-2n-1\right)} \end{aligned} \tag{38 }$$

The orthogonality of the functions $\psi(z)$[1]

$$N_m N_n \int_{-\infty}^{\infty} \psi_m(z)\,\psi_n(z)\,dr = \frac{1}{a} N_m N_n \int_0^\infty \psi_m(z)\cdot\psi_n(z)\frac{dz}{z} = \delta_{mn} \tag{39}$$

follows from the Schroedinger equation and the fact that $\psi(z)$ vanishes both when $z=0$ and z is infinite. It can also be verified by actually carrying out the integration in (39) with the help of the gamma function (35).

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[2] The limits of integration should be $r=0$ and $r=\infty$, corresponding to $z=2ae^{ar_0}$ and $z=0$ respectively. Since the function $\psi(z)$ in (27) decreases exponentially with z, there is little error in replacing the limit $z=2ae^{ar_0}$ by ∞.

To obtain the selection rule for the oscillator, we have to consider the matrix element of the electric moment, namely,

$$\mathfrak{M}(m\,;n)\propto\int_{-\infty}^{\infty} \psi_m(z) r\, \psi'_n(z)\, dr = \frac{1}{a} \int_{0}^{\infty} \psi'_m(z)\, \psi_n(z)\, log\left(\frac{z}{2a}\right) \frac{1}{z} dz. \tag{40}$$

It can be shown that this integral does not vanish in general for arbitrary values of m and n. Hence Δn is arbitrary and all quantum jumps, *i.e.*, all harmonics, are allowed.

C) Plane isotropic oscillator.[1]

Another type of vibration that finds frequent application in the theory of the vibration of molecules is the two dimensional vibration of a particle bound to a center of force such that the potential energy is

$$V = \tfrac{1}{2}\, k\, r^2 = 2\, \pi^2\, \nu^2\, \mu\, r^2$$

which is independent of φ, the angle the vector r makes with a fixed direction in the plane of motion. The kinetic energy is

$$T = \tfrac{1}{2}\, (\dot{r}^2 + r^2 \dot{\varphi}^2)$$

On introducing the dimensionless variable ϱ and the momenta p_ϱ and p_ϱ

$$\varrho = 2\pi \sqrt{\frac{\mu\nu}{h}}\, r, \qquad p_\varrho = \frac{\partial T}{\partial \dot{\varrho}}, \qquad p_\varphi = \frac{\partial T}{\partial \dot{\varphi}}, \tag{41}$$

the Hamiltonian becomes

$$H = T + V = \frac{2\pi^2 \nu}{h} \left[p_\varrho^2 + \frac{1}{\varrho^2}\, p_\varphi^2 \right] + \frac{h\nu}{2} \varrho^2, \tag{42}$$

and the Schrödinger equation is

$$\left[\frac{\partial^2}{\partial \varrho^2} + \frac{1}{\varrho} \frac{\partial}{\partial \varrho} + \frac{1}{\varrho^2} \frac{\partial^2}{\partial \varphi^2} + \frac{2E}{h\nu} - \varrho^2 \right] \psi = 0. \tag{43}$$

The eigenvalues of this equation are given by

$$E_n = (n + 1)\, h\nu, \tag{44}$$

and the eigenfunctions, which are periodic in φ and finite for all values of ϱ, are

$$\psi_{nl} = \frac{\sqrt{k\,!}}{\left[(l + k)!\right]^{\frac{8}{2}}}\, \frac{1}{\sqrt{\pi}}\, e^{\pm i l \varphi}\, e^{-\frac{\varrho^2}{2}}\, \varrho^l\, L_{l+k}^{l}(\varrho^2), \tag{45}$$

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[1] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931)

where $k = \frac{1}{2}(n-l)$, and L^l_{l+k} is the associated Laguerre polynomial of argument ϱ^2 and is the solution of the equation

$$\varrho^2 L''^{l}_{l+k} + (l + 1 - \varrho^2)\, L'^{l}_{l+k} + k\, L^l_{l+k} = 0 \tag{46}$$

The recurrence formula for the coefficients c_m in the expansion

$$L^l_{l+k}(\varrho^2) = \sum_{o}^{n-l} c_m\, \varrho^m$$

is

$$c_{m+2} = \frac{2m + 2l - 2n}{(m+2)(m+2+2l)}\, c_m, \tag{47}$$

and the explicit form for $L^l_{l+k}(\varrho^2)$ is

$$L^l_{l+k}(\varrho^2) = (-1)^{l+k}\frac{(l+k)!}{k!}\left[\varrho^{2k} - \frac{(l+k)k}{1!}\varrho^{2(k-1)} + \frac{(l+k)(l+k-1)k(k-1)}{2!}\varrho^{2(k-2)} \cdots\cdots\right]. \tag{48}$$

The properties of the functions ψ_{nl} are the following:

(i) For a given value (integer) of the quantum number n, the quantum number l can take $\frac{1}{2}n+1$ values, if n is even, corresponding to all values of k from 0 to $\frac{1}{2}n$, according to the relation $l = n - 2k$; and take $\frac{1}{2}(n+1)$ values, if n is odd, corresponding to all values of k from 0 to $\frac{1}{2}(n-1)$. For each value of $l \neq 0$, there are two wave functions differing from each other only in the factor $e^{\pm il\varphi}$. For $l=0$, there is only one wave function for each n. From these it follows that for each value of n (either even or odd), there are $n+1$ wave functions. Since the energy (44) is independent of the quantum number l, it follows that the state n is $(n+1)$-fold degenerate. We shall see immediately that the degeneracy comes from two sources: (1) the motion is isotropic in the plane of motion, and (2) the potential V has the particularly simple form $\frac{1}{2}k\, r^2$. That part of the degeneracy due to the second cause can be removed by introducing an anharmonic term in the potential. The degeneracy of states with $l \neq 0$, *i.e.*, the independence of the energy on the sign of l, however, can not be removed by any perturbation which is independent of φ. This is easily understood since physically this simply means that the energy can not be dependent on the sense of rotation of the vector ϱ in the absence of any external directional effect such as produced by a magnetic field.

(ii) Because of the factor $e_{\pm il\varphi}$, all integrals of the form

$$\int_0^{2\pi}\int_0^{\infty} \overset{*}{\psi}_{nl}\, \varrho^m\, \psi_{n'l'}\, \varrho d\varrho\, d\varphi = 0, \quad \text{for } l' \neq l. \tag{49}$$

The values of a few integrals that come in in perturbation calculations are given below:

$$\int_0^{\infty} \overset{*}{\psi}_{nl}\, \varrho^2\, \psi_{nl}\, \varrho d\varrho = n + 1,$$

$$\int_0^{\infty} \overset{*}{\psi}_{nl}\, \varrho^2\, \psi_{n+2,l}\, \varrho d\varrho = \tfrac{1}{2}\sqrt{(n+2)^2 - l^2},$$

$$\int_0^{\infty} \overset{*}{\psi}_{nl}\, \varrho^4\, \psi_{nl}\, \varrho d\varrho = \tfrac{1}{2}(3\,n^2 + 6\,n + 4 - l^2). \tag{50}$$

To obtain the selection rule for the plane harmonic oscillator, let us consider, for convenience, the matrix element of $\mathfrak{M}_x + i\,\mathfrak{M}_y$, where $\mathfrak{M}_x$ and $\mathfrak{M}_y$ are the components of the electric moment along two axes x and y in the plane of motion. As $\mathfrak{M}_x$ and $\mathfrak{M}_y$ are proportional to $x = r\cos\varphi$ and $y = r\sin\varphi$ respectively, we have

$$(\mathfrak{M}_x + i\,\mathfrak{M}_y)\,(nl;\, n'l') \propto \int_0^{2\pi}\int_0^{\infty} \overset{*}{\Psi}_{nl}\, \varrho e^{i\varphi}\, \Psi_{n'l'}\, \varrho d\varrho\, d\varphi,$$

which vanishes except when $l = l' \pm 1$. For $l = l' + 1$, integration over ϱ causes the integral to vanish except for $n = n' + 1$. For $l = l' - 1$, the integral vanishes except when $n = n' - 1$. Hence the selection rules are

$$\Delta n = \pm 1, \qquad \Delta l = \pm 1. \tag{51}$$

Next let us take a plane anharmonic oscillator. As the potential energy must be an even function of ϱ and must be independent of φ, we may consider the effect of anharmonic term

$$\lambda\, V_1 = \lambda\, h\, k_1\, \varrho^4.$$

The energy change given by the diagonal element of V_1 according to (15) and (50) is

$$E'_{nl} = \tfrac{1}{2}\, k_1\, (3n^2 + 6n + 4 - l^2)\, h\nu, \qquad (52$$

which depends on the numerical values but not the sign of l.

To obtain the selection rules for the anharmonic oscillator, we must examine the matrix elements of $x + iy = re^{i\varphi}$ with respect to the wave functions of the anharmonic oscillator, namely, in quantities up to the first power of λ,

$$\Psi_{nl} = \Psi^{\circ}_{nl} + \lambda \sum_{kl'}{}' a^{nl}_{kl'} \Psi^{\circ}_{kl'},$$

where

$$a^{nl}_{kl'} = \frac{\int\limits_{0}^{2\pi} \int\limits_{0}^{\infty} \overset{*}{\Psi}{}^{\circ}_{nl} V_1 \Psi^{\circ}_{kl'} \varrho d\varrho d\varphi}{E^{\circ}_{n} - E^{\circ}_{k}}$$

Since the perturbing potential must be independent of φ, the coefficients $a^{nl}_{kl'}$ will vanish for $l' \neq l$. Hence the wave functions Ψ_{nl} of the anharmonic oscillator depend on φ in exactly the same way (*i.e.*, through the same factor $e^{\pm il\varphi}$) as the wave functions of the harmonic oscillator. From this it follows that the selection rule for l remains the same as before, namely, $\Delta l = \pm 1$. The selection rule for n can be obtained by substituting (55) into an expression of the form (23). It is found that up to the first power in λ, harmonics with $\Delta n = \pm 3$ will also be allowed in the spectrum of the anharmonic oscillator.

D) Space isotropic oscillator

The Schrödinger equation for a 3-dimensional harmonic oscillator

$$\Delta\Psi + \frac{8\pi^2\mu}{h^2}\left[E - k\, r^2\right]\Psi = 0$$

separates into three ordinary differential equations on putting

$$\Psi = e^{im\varphi} P^{m}_{l}(\cos\vartheta)\frac{1}{r}\psi(r),$$

where ψ satisfies the equation

$$\frac{d^2\psi}{d\varrho^2} + \left[\frac{2E}{h\nu} - \varrho^2 - \frac{l(l+1)}{\varrho^2}\right]\psi = 0, \tag{53}$$

in which $\varrho = 2\pi\sqrt{\frac{\mu\nu}{h}} \cdot r$ as in (41). The solution of (53) can be put in the form

$$\psi(\varrho) = e^{-\frac{\varrho^2}{2}} \varrho^{l+1} F(\varrho)$$

where $F(\varrho)$ is the solution of

$$F'' + 2\left(\frac{l+1}{\varrho} - \varrho\right)F' + \left[\frac{2E}{h\nu} - 2l - 3\right]\omega = 0$$

The method of solving the equation by polynomials leads to the eigenvalues

$$E = h\nu(j + l + \tfrac{3}{2}) = h\nu(v + \tfrac{3}{2}) \tag{54}$$

where v is a positive integer $\geqq l$. This differs from the energy expressions for the linear and the plane harmonic oscillators in the zero point energy $\frac{3}{2} h\nu$. The solution of the Schrödinger equation is now

$$e^{im\varphi} P_l^m (\cos \vartheta)\, e^{-\frac{\varrho^2}{2}} \varrho^l F(\varrho), \tag{55}$$

where $F(\varrho) = \Sigma a_k \varrho^k$ is given by the recurrence formula

$$a_{k+2} = \frac{2(k + l - v)}{(k + 2)(k + 2l + 3)} a_k$$

Since the energy of the oscillator is independent of the quantum numbers m and l, and since for a given value of l, m can take on $2l+1$ values while for a given value of v, l can take the values v, $v-2$, $v-4$,.... to 1 or 0 according as whether v is odd or even, it follows that each vibrational state v is degenerate, the degree of degeneracy being given by

$$\tfrac{1}{2} (v + 1)(v + 2). \tag{56}$$

This degeneracy is the result of (1) the isotropy of the vibration and (2) the harmonic potential. A part of this degeneracy can be removed by introducing an anharmonic term in the potential such as $V_1 = k_1 \varrho^4$, The energy change due to such a perturbing potential is given by the matrix element V_1 $(v, l, m; v, l, m)$. It can be shown that this is given by

$$V'(v, l; v, l) = \tfrac{1}{2} k_1 \left[3(v + \tfrac{3}{2})^2 - (l + \tfrac{1}{2})^2 + 1\right]. \tag{57}$$

This splits the $\frac{1}{2}(v+1)(v+2)$-fold degenerate state into a number of $\frac{1}{2}(v+2)$ levels if v even, and $\frac{1}{2}(v+1)$ levels if v odd, which are $(2v+1)$-, $(2v-3)$-, $(2v-7)$-, ...1 or 3-fold degenerate, according as whether v is even or odd.

If the oscillator is perturbed by a potential which is tetrahedrally symmetrical instead of spherically symmetrical, as in the case of certain vibrations in such molecules as CH_4, it can be shown that a state v is split into a number of levels none of which is more than 3-fold degenerate.[1] In this case, the perturbation calculation can be more conveniently carried out by using rectangular coordinates in the Schrödinger equation. The number of sub-levels for $v \leqq 4$ is shown in Table I.

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[1] D. M. Dennison and S. B. Ingram, Phys. Rev. 36, 1451, (1930).

$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$E(1)$	$E(3)$	$E(3)$ $E(2)$ $E(1)$	$E(3)$ $E(3)$ $E(3)$ $E(1)$	$E(3)$ $E(3)$ $E(3)$ $E(2)$ $E(2)$ $E(1)$ $E(1)$

Table I. Energy levels of tetrahedral YX_4 molecules. Numbers in parentheses are the degrees of degeneracy.

§2. Vibrations of Molecules: Initial Approximation

Suppose a classical treatment of the normal vibrations of a molecule has already been carried through so that in the normal coordinates, the kinetic and the potential energies are given by equations (7) of Chap. II,

$$2T = \Sigma \dot{X}_i^2 , \qquad 2V = \Sigma \lambda_i X_i^2,$$

where $\lambda_i = 4\pi^2\omega_i^2$, and the ω's are the zeroth order frequencies. On introducing the dimensionless variables and their momenta

$$y_i = 2\pi \sqrt{\frac{\omega_i}{h}}\, X_i , \qquad p_i = \frac{\partial T}{\partial \dot{y}_i}, \tag{58}$$

the Hamiltonian becomes

$$H = \frac{2\pi^2}{h} \Sigma \omega_i p_i^2 + \frac{h}{2} \Sigma \omega_i y_i^2.$$

The Schroedinger equation $H\Psi = E\Psi$ for the system can be separated by assuming

$$\left.\begin{aligned} \Psi &= \psi_{v_1}(y_1) \cdot \psi_{v_2}(y_2) \cdots\cdots \cdot \psi_{v_n}(y_n) \\ E &= E_{v_1} + E_{v_2} + E_{v_3} + \cdots\cdots + E_{v_n} \end{aligned}\right\} \tag{59}$$

and

into n equations of the type

$$\frac{d^2\psi_{v_i}}{dy_i^2} + \left[\frac{2E_i}{h\omega_i} - y_i^2 \right] \psi_{v_i} = 0, \tag{60}$$

which is identical with equation (1) for a simple harmonic oscillator. The eigenvalues and the eigenfunctions of (60) are given by (2) and (10). The total energy of vibration of the molecule is

$$E = \Sigma (v_i + \tfrac{1}{2}) h\omega_i. \tag{61}$$

A) Absorption spectrum

To obtain the selection rules in emission and absorption, it is necessary to examine the matrix elements of the components of the electric moment along certain fixed directions in space. Consider for example the x component of the electric moment as given in (31) of Chap. II, namely,

$$\mathfrak{M}_x = \mathfrak{M}_x^0 + \sum_i \left(\frac{\partial \mathfrak{M}_x}{\partial X_i}\right)_0 X_i + \cdots\cdots.$$

The matrix element of $\mathfrak{M}_x$ associated with the transition between the states given by the quantum numbers $v_1, v_2, \ldots v_n$ and $v_1', v_2', \ldots v_n'$ is, in a first approximation,

$$\mathfrak{M}_x(v_1\cdots v_n; v_1'\cdots v_n') = \mathfrak{M}_x^0 \int \Psi^*_{v_1\cdots v_n} \Psi_{v_1'\cdots v_n'}\, dX_1\cdots dX_n$$
$$+ \sum_i \left(\frac{\partial \mathfrak{M}_x}{\partial X_i}\right)_0 \int \Psi^*_{v_1\cdots v_n} X_i \Psi_{v_1'\cdots v_n'}\, dX_1\cdots dX_n. \quad (62)$$

The term in $\mathfrak{M}_x^0$ vanishes except when $v_i = v_i'$ for all values of i, and hence gives rise to no emission or absorption during the transition. The integral in the second term vanishes except when

$$v_1 = v_1', \cdots \cdots v_{i-1} = v'_{i-1},\ v_i = v'_i \pm 1,\ v_{i+1} = v'_{i+1}, \cdots \cdots v_n = v'_n. \quad (63)$$

on account of the orthogonality properties of the wave functions $\psi_{v_i}(y_i)$. Entirely similar results hold for the y and the z components of the electric moment. Hence in this approximation, only the fundamental frequencies may appear in the spectrum, there being no harmonics nor combinations of the fundamentals. As to whether a particular vibration is active, and if so, what are the directions of the change of the electric moment, one must apply the same considerations of the symmetry properties of the vibrations as in §6 of Chap. II.

In the following section, it will be shown that the appearance of harmonics and combination bands can be accounted for by taking into consideration the anharmonicity of the vibrations, and that the selection rules for them can be obtained also from the symmetry properties of the vibrations.

B) Raman spectrum

To understand the vibrational Raman effect of a molecule, it is necessary to consider the scattering process in the quantum theory. A detailed treatment has been given by Placzek[1]. In the following, we shall give a brief discussion and refer the reader to the work of Placzek and of Breit[1].

Consider a molecule with energy states E_j and the corresponding eigenfunctions $\Psi_j = \psi_j\, e^{-2\pi i \frac{E_j}{h} t}$ which satisfy the Schrödinger time dependent wave equations

$$\left(H_0 + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\Psi = 0, \qquad \left(\overset{*}{H}_0 - \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\overset{*}{\Psi} = 0. \tag{64}$$

When perturbed by a light wave whose electric vector is

$$\mathcal{E} = A\, e^{2\pi i \nu t} + \overset{*}{A}\, e^{-2\pi i \nu t}, \tag{65}$$

the wave equations for the system become

$$\left(H_0 - \mathcal{M}\mathcal{E} + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\Psi = 0, \qquad \left(\overset{*}{H}_0 - \mathcal{M}\mathcal{E} - \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\overset{*}{\Psi} = 0 \tag{66}$$

where $\mathcal{M}$ is the electric moment of the system. Let the first order change in the eigen function of the state n be Ψ'_n so that

$$\Psi_n = \Psi_n^0 + \Psi'_n. \tag{67}$$

On neglecting small quantities of the second order, equations (66) become

$$\left(H_0 + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\Psi'_n = (\mathcal{M}\mathcal{E})\Psi_n^0, \quad \left(\overset{*}{H}_0 - \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\overset{*}{\Psi}{}'_n = (\mathcal{M}\mathcal{E})\,\overset{*}{\Psi}{}_n^0 \,.. \tag{68}$$

Let us assume that

$$\Psi'_n = \psi_n^+\, e^{-\frac{2\pi i}{h}(E_n + h\nu)t} + \psi_n^-\, e^{-\frac{2\pi i}{h}(E_n - h\nu)t}, \tag{69}$$

and a similar expression for the complex conjugate $\overset{*}{\Psi}{}'_n$. On substituting these into (68) and equating terms having the same time factor, one obtains

$$\begin{aligned} &\Big[H_0 - (E_n + h\nu)\Big]\psi_n^+ = (A\mathcal{M})\psi_n^0, \qquad &&\Big[H_0 - (E_n - h\nu)\Big]\psi_n^- = (\overset{*}{A}\mathcal{M})\psi_n^0, \\ &\Big[\overset{*}{H}_0 - (E_n + h\nu)\Big]\overset{*}{\psi}{}_n^+ = (\overset{*}{A}\mathcal{M})\overset{*}{\psi}{}_n^0, \qquad &&\Big[\overset{*}{H}_0 - (E_n - h\nu)\Big]\overset{*}{\psi}{}_n^- = (A\mathcal{M})\overset{*}{\psi}{}_n^0. \end{aligned} \tag{70}$$

To solve these equations, let us expand the right-hand members of these equations in terms of the orthogonal set of eigen functions of the unperturbed system,

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[1] G. Placzek, Marx's *Handbuch der Radiologie*, Bd VI/2, 2nd ed.; also G. Breit, Rev. Mod. Phys. 4, 504, (1932); 5, 91, (1933), for a detailed discussion of the quantum theory of dispersion.

$$(A\mathcal{M})\,\psi^\circ_n = \sum_r (A\mathcal{M})_{nr}\,\psi^\circ_r\ , \qquad etc., \tag{71}$$

where

$$(A\mathcal{M})_{nr} = \int \overset{*}{\psi}{}^\circ_r A\mathcal{M}\ \psi^\circ_n\ d\tau. \tag{72}$$

Then it follows from (64) and the Hermitian property $M_{ij} = \overset{*}{M}_{ji}$ that

$$\psi^+_n = \sum_r \frac{(A\mathcal{M})_{nr}}{E_r-(E_n+h\nu)}\,\psi^\circ_r\ , \quad \psi^-_n = \sum_r \frac{(\overset{*}{A}\mathcal{M})_{nr}}{E_r-(E_n-h\nu)}\,\psi^\circ_r\ ,$$

$$\overset{*}{\psi}{}^+_n = \sum_r \frac{(\overset{*}{A}\mathcal{M})_{rn}}{E_r-(E_n+h\nu)}\,\overset{*}{\psi}{}^\circ_r\ , \quad \overset{*}{\psi}{}^-_n = \sum_r \frac{(A\mathcal{M})_{rn}}{E_r-(E_n-h\nu)}\,\overset{*}{\psi}{}^\circ_r\ . \tag{73}$$

Consider now the matrix element of the x component of the electric moment of the system associated with the state n and another state k (When we confine our attention to the vibrational states alone, n stands for the totality of the vibrational quantum numbers $v_1, v_2, \ldots . v_n$ in (59). Similarly for k). Neglecting small quantities of the second order again, one obtains

$$\begin{aligned}\mathcal{M}_x(k,n) &= \int (\overset{*}{\Psi}{}^\circ_k + \overset{*}{\Psi}{}'_k)\,\mathcal{M}_x(\Psi^\circ_n + \Psi'_n)\,d\tau = \mathfrak{M}_x(n,k)\,e^{-2\pi i\nu_{nk}t}\\ &+\frac{1}{h}\sum_r\left[\frac{(A\mathcal{M})_{nr}(\mathcal{M}_x)_{rk}}{\nu_{rn}-\nu}+\frac{(\mathcal{M}_x)_{nr}(A\mathcal{M})_{rk}}{\nu_{rk}+\nu}\right]e^{-2\pi i(\nu_{nk}+\nu)t}\\ &+\frac{1}{h}\sum_r\left[\frac{(\overset{*}{A}\mathcal{M})_{nr}(\mathcal{M}_x)_{rk}}{\nu_{rn}+\nu}+\frac{(M_x)_{nr}(\overset{*}{A}\mathcal{M})_{rk}}{\nu_{rk}-\nu}\right]e^{-2\pi i(\nu_{nk}-\nu)t}\end{aligned} \tag{74}$$

Here in the spirit of the correspondence principle, Klein[2] assumed that the component of the electric moment $\mathfrak{M}(i,j)\,e^{-2\pi i\nu_{ij}t}$ is zero if $\nu_{ij} < 0$ and is equal to that associated with

$$\mathfrak{M}(i,j)\,e^{-2\pi i\nu_{ij}t} + \overset{*}{\mathfrak{M}}(i,j)\,e^{2\pi i\nu_{ij}t}$$

if $\nu_{ij} > 0$. Thus the first term in (74) corresponds to the spontaneous emission of the state n to the state k ($E_n > E_k$). The second term represents the radiation of frequency $\nu_{nk}+\nu$ for $\nu_{nk}+\nu > 0$. Here we distinguish three cases, namely, $E_n > E_k$, $E_n < E_k$ and $E_n = E_k$. These are readily seen to correspond to the anti-Stokes, the Stokes and the undeviated line respectively of the scattered radiations, as shown in Fig. **11**, (a), (b), (c).

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[2] O. Klein, Zeits. f. Physik 41, 407, (1927).

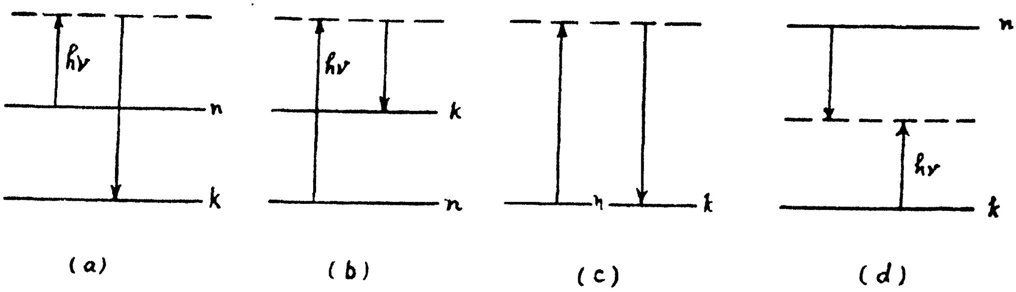

Fig. 11

In the case $E_n = E_k$, we again distinquish between $k=n$ and $k \neq n$. For $k=n$, the first term in (74) is simply the x component of the permanent dipole moment of the system in the state n, while the second and the third terms can be put in the form

$$\mathcal{M}'_x(n,n) = \mathfrak{M}_x(n,n)\, e^{-2\pi i\nu t} + \overset{*}{\mathfrak{M}}_x(n,n)\, e^{2\pi i\nu t} \qquad (75)$$

where

$$\mathfrak{M}_x(n,n) = \frac{A}{h} \sum_r \left[\frac{(\mathcal{M})_{nr}(\mathcal{M}_x)_{rn}}{\nu_{rn} - \nu} + \frac{(\mathcal{M}_x)_{nr}(\mathcal{M})_{rn}}{\nu_{rn} + \nu} \right], \qquad (76)$$

(75) represents the coherent part of the Rayleigh scattering since the matrix element $\mathcal{M}'_x(n,n)$ is independent of any arbitrary phase factor in the eigen function $\psi_n^0 e^{-2\pi i\left(\frac{E_n}{h} t - \delta_n\right)}$ and the scattered radiatoins from different molecules are in a condition to produce interference. For $n \neq k$ but $E_n = E_k$ so that the two states are degenerate, the martix element $\mathcal{M}'_x(n\cdot k)$ will contain a factor $e^{-2\pi i(\delta_n - \delta_k)}$ which is different for different molecules, the scattered radiations are not in a condition to produce interference and are called incoherent.

The third term in (74) represents radiations of frequency $\nu_{nk} - \nu$ if $\nu_{nk} - \nu > 0$. In this case, the state n must be an excited state, as shown in (d) of Fig. 11.

We are here chiefly interested in the Raman scattering given by the second term of (74). The intensity of the scattered radiation is given by

$$I_{nk} = \frac{64\pi^4(\nu + \nu_{nk})^4}{3c^3} \sum_x \left| \mathfrak{M}'_x(n,k) \right|^2,$$

where

$$\begin{aligned}\mathfrak{M}'_x(n,k) &= \frac{1}{h}\sum_{\sigma}^{x,y,z}\sum_r\left[\frac{(\mathcal{M}_\sigma)_{nr}(\mathcal{M}_x)_{rk}}{\nu_{rn}-\nu}+\frac{(\mathcal{M}_x)_{nr}(\mathcal{M}_\sigma)_{rk}}{\nu_{rk}+\nu}\right]A_\sigma \\ &= \sum_\sigma (\alpha'_{x\sigma})_{nk}A_\sigma \end{aligned} \tag{77}$$

The quantities $(\alpha'_{x\sigma})$ defined in (77) are seen to transform as the products of the components of two vectors $(A_\sigma \mathcal{M}_\sigma)$ and $(\mathcal{M}_x)$, and are hence the components of a tensor. The above relations between the components of the induced electric moment $\mathfrak{M}'$ and the inducing field vector A are the same as those in (39) of Chap. II.

From (77), it follows that a necessary condition for a Raman line ν_{nk} to appear at all is that a state r exists such that the matrix elements of the electric moments associated with r and n and with r and k do not vanish at the same time. The existence of such states r, however, is not sufficient, since by chance the matrix elements $\mathfrak{M}'(n,k)$ may still have vanishingly small values when the summation over all the intermediate states r is made in (77).

The selection rules for the vibrational Raman spectrum of a molecule can be obtained from a study of the scattering formula (77). It is seen that while the selection rules for the absorption spectrum are determined by the matrix elements of the dipole moment (62), they are determined, for the Raman spectrum, by the matrix elements of the components of the polarizability tensor α. Hence the selection rules are in general different for the two spectra. A particularly simple example illustrating this difference is found in molecules possessing a center of symmetry. Consider two states n and k. The frequency ν_{nk} will be active in absorption (or emission) if the wave functions of the two states have opposite symmetry characters, *i.e.*, one is symmetrical and the other antisymmetrical with respect to a reflection about the symmetry center. This follows since the dipole moment of the molecule is a vector, and the integration in (62) is taken over all values of the coordinates. On the other hand, for the frequency ν_{nk} to appear in the Raman spectrum, the wave functions of the two states must have the same symmetry character since the polarizability α is a tensor and is symmetrical with respect to the reflection. From these it follows that in such molecules, frequencies that are active in absorption are not active in the Raman spectrum, and vice versa. In molecules possessing more than one elements of symmetry, the selection rules can be obtained from a consideration of the symmetry properties of the wave functions of the different states with respect to the symmetry operations (reflection about a center, rotation about an axis, etc.). Selection rules for molecular models of various symmetries have been given by Placzek.[1] In Chap. V, we shall give them for those models corresponding to the actual molecules.

An interesting special case of the scattering formula (74) is when $\nu=0$, *i.e.*, when the molecule is in a static field. In this case, the matrix elements of the components of the induced dipole moment associated with the states n and k have the frequency ν_{nk}. Thus radiations of the frequency ν_{nk} can be absorbed or emitted by the molecule even when the dipole transition between the two states is forbidden for the unperturbed molecule. This suggests the possibility of observing inactive transitions in the infrared absorption spectrum,[3] in the same way as forbidden transitions in atomic spectrà are observed in Stark effect.[4] In fact in both cases, the activity of these transitions in the electric field is due to the induced electric moment of the system by the electric field. Hence we may regard the appearance of Raman lines in the limit of $\nu=0$ for the exciting radiation as a Stark effect of the vibrational spectra. The frequency shifts produced by the external electric field are given by (16) in which the perturbing potential is $\mathfrak{M}\mathcal{E}$.

Having justified the introduction of the polarizability tensor in (77), let us consider the scattering process by a molecule. The intensity of the scattered radiations is determined by the matrix elements of the induced electric moment. For a transition between two states defined by the quantum numbers $v_1, v_2, \ldots. v_n$ and $v'_1, v'_2, \ldots. v'_n$, the martix element of the x component of the induced electric moment under the action of the electric field $\mathcal{E}'_j=\mathcal{E}^\circ_j\, e^{2\pi i\nu t}$ of the incident radiation is, in a first approximation, given by (45) of Chap. II,

$$\begin{aligned}\mathfrak{M}_x(v_1\cdots v_n;\, v'_1\cdots v'_n) &= e^{2\pi i\nu t}\sum \mathcal{E}^\circ_j\,(\alpha_{xj})^\circ\int \overset{*}{\Psi}_{v_1\cdots v_n}\Psi_{v'_1\cdots v'_n}\,dX_1\cdots dX_n\\ &+ e^{2\pi i\nu t}\sum_j\sum_k \mathcal{E}^\circ_j\left(\frac{\partial \alpha_{xj}}{\partial X_k}\right)_\circ\int \overset{*}{\Psi}_{v_1\cdots v_n}X_k\Psi_{v'_1\cdots v'_n}\,dX_1\cdots dX_n \qquad (78)\end{aligned}$$

where the summation in j is taken over $j=x,\ y,\ z$, and

$$\Psi_{v_1\cdots v_n}=\prod_k \psi_{v_k}(X_k,t), \qquad \psi_{v_k}(X_k,t)=\psi_{v_k}(X_k)\,e^{-2\pi i\frac{E_k}{h}t}, \qquad (79)$$

the $\psi_{v_k}(X_k)$ being the orthogonal Hermitian functions (10). The terms containing $(\alpha_{xy})^{\circ}$ do not vanish only when $v_i = v_i'$ for all values of *i*, *i.e.*, when there is no change in the vibrational state. The integral in the second term on the right vanishes except when the quantum numbers satisfy the condition (63). Entirely similar results hold for the other components of the induced electric moment. The first term in (64) gives the classical Rayleigh scattering, while the second term in (64) gives the Stokes and the anti-Stokes Raman lines with the frequencies $\nu - \nu_k$ and $\nu + \nu_k$. It is seen from (78) that in the approximation employed here, only the fundamental frequencies of the molecule will appear in the Raman effect. The question as to whether a particular vibration is active, and if so, what are the polarization characters of the scattered radiation, is again determined by the values of the coefficients $\left(\frac{\partial\alpha_{ij}}{\partial\xi_k}\right)_0$, for which the considerations of §6, Chap. II hold. The appearance of harmonic and combination frequencies can be shown to arise from higher order effects. This accounts for the fact that in general the harmonic and combination frequencies are not observed and in a few cases they are observed only with low intensities.[5]

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[3] E. U. Condon, Phys. Rev. 41, 759, (1932).

[4] The $^2S-m^2S$ and the $^2S-m^2D$ series are observed in the inverse Stark effect of the spectra of the alkalie metal atoms, for example.

The anti-Stokes line of frequency $\nu + \nu_k$ has its origin in molecules that have already been excited to the vibrational state $v_k = 1$ when the process of scattering takes place. Its very much lower intensity compared with that of the corresponding Stokes lines is due to the much smaller, by the Boltzmann factor $e^{-\frac{h\nu_k}{kT}}$, population of the excited state under ordinary experimental conditions. According to the classical theory of §5, Chap. II, however, it would not be possible to understand the difference in the intensities of the Stokes and the anti-Stokes lines, for there the idea of the different energy states does not come in at all.

§3. Vibrations of Molecules: Higher Approximations

It is shown in the last section that if the vibrations of a molecule are strictly simple harmonic, no overtones nor combinations of the fundamental frequencies would be observed in the absorption and the Raman spectra. It is found, however, that overtones and combination bands are actually observed in the absorption spectra of practically all the molecules that have been studied, and that the energies of vibrations can be empirically represented by including in the expression (61) terms that are proportional to the squares and the products of the various vibrational quantum numbers. The explanation of these is to be found, just as in the case of a single oscillator in §1, in the fact that the motions of the atoms in a molecule are not strictly simple harmonic. Hence our next problem is to study the effect, on both the energy and the selection rules, of the anharmonicity of the vibrations.

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[5] Cases in which the harmonic of a fundamental appears in the Raman spectrum with considerable intensity are found when there is the quantum mechanical effect of resonance between the harmonic and another fundamental. See section 4, B of this chapter.

A) Normal coordinate method

A natural method for including the effect of anharmonicity of the vibrations is the perturbation method. Unless the motions are very widely different from being simple harmonic, the assumption of a quadratic potential can be expected to form a good initial approximation on the basis of which the effect of anharmonicity can be determined by calculating the perturbations due to the higher order terms in the potential. In theory, such a perturbation calculation can be carried out for any given molecule. Because, however, of the lengthy calculations involved for any but the simplest of molecules, and also because of the practical difficulties in securing the necessary experimental data for the analysis to be useful, such calculations have been carried out for only a few molecules. We shall here consider in detail only the linear symmetrical YX_2 model not only because it sufficiently illustrates the method but also because of its successful application to the carbon dioxide molecule.[1]

We shall choose the coordinates q, r and z defined in §6, equs. (48) of Chap. II. It can be easily shown that in these coordinates the kinetic and the potential energies are

$$\begin{aligned} T &= \tfrac{1}{4}\, m\, \dot{q}^2 + \tfrac{1}{2}\, \mu\, (\dot{z}^2 + \dot{r}^2 + r^2 \dot{\varphi}^2) \\ V &= m\pi^2 \omega_1^2 q^2 + 2\mu\pi^2 \omega_2^2 r^2 + 2\mu\pi^2 \omega_3^2 z^2, \end{aligned} \qquad (80)$$

where $\mu = 2mM/(M+2m)$. On introducing the dimensionless coordinates

$$\sigma = 2\pi\sqrt{\frac{\omega_1 m}{2h}} \cdot q \; , \quad \xi = 2\pi\sqrt{\frac{\omega_3 \mu}{h}} \cdot z \; , \quad \varrho = 2\pi\sqrt{\frac{\omega_2 \mu}{h}} \cdot r \qquad (81)$$

and their momenta given by expressions similar to (56), equations (80) become

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[1] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931); Phys, Rev. 41, 304, (1932); A. Adel and D. M. Dennison, Phys. Rev. 43, 716, (1933).

$$T = \frac{2\pi^2}{h}\left[\omega_1 p_\sigma^2 + \omega_2 p_\varrho^2 + \omega_2 \frac{1}{\varrho^2} p_\varphi^2 + \omega_3 p_\xi^2\right],$$

$$V = \frac{h}{2}\left[\omega_1 \sigma^2 + \omega_2 \varrho^2 + \omega_3 \xi^2\right]. \tag{81a}$$

The Schrödinger equation then separates into three equations, one of the form (43) and two of the form (60). The eigenvalues and the eigenfunctions are given by (44), (45), (2) and (10), and for the whole system, one obtains

$$E^{\circ}_v = (v_1 + \tfrac{1}{2})\, h\omega_1 + (v_2 + 1)\, h\omega_2 + (v_3 + \tfrac{1}{2})\, h\omega_3,$$

$$\Psi_v = \psi^{\circ}_{v_1}(\sigma)\cdot \psi^{\circ}_{v_2 l}(\varrho, \varphi)\cdot \psi^{\circ}_{v_3}(\xi), \tag{82}$$

where v stands for the totality of the quantum numbers v_1, v_2, l, v_3.

If it now be assumed that the molecule is perturbed by anharmonic potentials that have the same symmetry as the geometrical symmetry of the molecule, namely, they must be even functions of r and z, and must be independent of the angle φ,

$$\lambda V_1 = \lambda h\, [a\sigma^3 + b\sigma\varrho^2 + c\sigma\xi^2], \tag{83}$$

$$\lambda^2 V_2 = \lambda^2 h\, [d\sigma^4 + e\varrho^4 + f\xi^4 + g\,\sigma^2\varrho^2 + i\,\varrho^2\xi^2 + j\,\sigma^2\xi^2], \tag{84}$$

then one finds that the first order change in energy is zero,

$$\lambda E'_v = \lambda V_1(v_1 v_2 v_3 l;\, v_1 v_2 v_3 l) = \lambda \int \overset{*}{\Psi}_v\, V_1\, \Psi_v\, d\tau = 0,$$

where $d\tau = d\sigma\, d\xi\, d\varphi\, \varrho d\varrho$. The second order energy change is given by an expression similar to (16), namely,

$$\lambda^2 E''_v = \lambda^2 \int \overset{*}{\Psi}_v\, V_2 \Psi_v\, d\tau + \lambda^2 \Sigma' \frac{[\int \overset{*}{\Psi}_v\, V_1\, \Psi_{v'}\, d\tau]^2}{E^{\circ}_v - E^{\circ}_{v'}} \tag{85}$$

in which the summation is taken over all possible sets of the quantum numbers v_1', v_2', l', v_3', not all of which are identical with v_1, v_2, l, v_3. The non-vanishing non-diagonal matrix elements of V_1, twelve in number, are the following:

$$(V_1)^{v_1\pm 1, v_2, v_3}_{v_1, \quad v_2, v_3} \qquad (V_1)^{v_1\pm 3, v_2, v_3}_{v_1, \quad v_2, v_3} \qquad (V_1)^{v_1\pm 1, v_2\pm 2, v_3}_{v_1, \quad v_2, \quad v_3} \qquad (V_1)^{v_1\pm 1, v_2, v_3\pm 2}_{v_1, \quad v_2, v_3}$$

All these matrix elements can be evaluated by referring to (20) and (50). On writing the energy $E = E^{\circ} + E' + E''$ in the form

$$E = x' + \nu_1 v_1 + \nu_2 v_2 + \nu_3 v_3 + x_{11} v_1^2 + x_{22} v_2^2 + x_{33} v_3^2$$
$$+ x_{12} v_1 v_2 + x_{23} v_2 v_3 + x_{13} v_1 v_3 + x_{ll} l^2, \tag{86}$$

one obtains the following relations

$$
\begin{aligned}
x' &= \text{constant} \\
\nu_1 &= \omega_1 + \tfrac{3}{2}\,d + g + \tfrac{1}{2}\,j - \frac{3a}{\omega_1}\left[\frac{5a}{4} + b + \frac{c}{2}\right] - \frac{b^2}{2(\omega_1+2\omega_2)} + \frac{b^2}{2(\omega_1-2\omega_2)} \\
&\quad - \frac{c^2}{4(\omega_1+2\omega_3)} + \frac{c^2}{4(\omega_1-2\omega_3)}, \\
\nu_2 &= \omega_2 + 3\,e + \tfrac{1}{2}g + \tfrac{1}{2}\,i - \frac{b}{\omega_1}\left[\frac{3a}{2} + b + \frac{c}{2}\right] - \frac{b^2}{2(\omega_1+2\omega_2)}, \\
\nu_3 &= \omega_3 + \tfrac{3}{2}\,f + \tfrac{1}{2}\,j + \;i - \frac{c}{\omega_1}\left[\frac{3a}{2} + b + \frac{c}{2}\right] - \frac{3c^2}{8(\omega_1+2\omega_3)} + \frac{c^2}{8(\omega_1-2\omega_3)}, \\
x_{11} &= \tfrac{3}{2}\,d - \frac{15}{4}\,\frac{a^2}{\omega_1}, \\
x_{22} &= \tfrac{3}{2}\,e - \frac{b^2}{2\omega_1} - \frac{b^2}{8\,(\omega_1+2\omega_2)} - \frac{b^2}{8\,(\omega_1-2\omega_2)}, \\
x_{33} &= \tfrac{3}{2}\,f - \frac{c^2}{2\omega_1} - \frac{c^2}{8\,(\omega_1+2\omega_3)} - \frac{c^2}{8\,(\omega_1-2\omega_3)}, \\
x_{ll} &= \;e - \frac{b^2}{2\omega_1} - x_{22} \\
x_{12} &= \;g - \frac{3ab}{\omega_1} - \frac{b^2}{2\,(\omega_1+2\omega_2)} + \frac{b^2}{2\,(\omega_1-2\omega_2)}, \\
x_{13} &= \;j - \frac{3ac}{\omega_1} - \frac{c^2}{2\,(\omega_1+2\omega_3)} + \frac{c^2}{2\,(\omega_1-2\omega_3)}, \\
x_{23} &= \;i - \frac{bc}{\omega_1}.
\end{aligned}
\tag{87}
$$

From these relations, one obtains, on elimination,[1]

$$
\begin{aligned}
\omega_1 &= \nu_1 - \;x_{11} - \;x_{12} - \tfrac{1}{2}x_{13}, \\
\omega_2 &= \nu_2 - 2x_{22} - \tfrac{1}{2}x_{12} - \tfrac{1}{2}x_{23}, \\
\omega_3 &= \nu_3 - \;x_{33} - \;x_{23} - \tfrac{1}{2}x_{13}.
\end{aligned}
\tag{88}
$$

With sufficient appropriate experimental data on the harmonic and combination bands of the molecule, the coefficients ν_1, ν_2, ν_3, $x_{11} \ldots . x_{33}, \ldots .$ x_{23} in the energy expression (86) can be determined. Equations (88) then enable one to obtain the zeroth order frequencies ω's, and from (87) one can determine the constants a, $b, \ldots . i$, j, thus defining the potential function of the molecule up to the second order.[2] Application of the results here to the carbon dioxide molecule will be taken up in Chap. V.

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[1] The paper of Adel and Dennison, Phys. Rev. 43, 716, (1933) contains a number of errors. Equations (87) and (88) given here are the corrected results.

To obtain the selection rules for the harmonic and the combination bands of the molecule, it is necessary to consider the wave functions of the system of anharmonic oscillators, namely,

$$\Psi_v = \Psi_v^\circ + \sum_{v'}{}' \frac{\int \overset{*}{\Psi}{}_v^\circ \, V_1 \, \Psi_{v'}^\circ \, d\tau}{E_v^\circ - E_{v'}^\circ} \Psi_{v'}^\circ , \tag{89}$$

where V_1 is the perturbation potential and v stands for v_1, v_2, l, v_3. Since the anharmonic potential V_1 must be even in r and z, and independent of φ, it follows from the properties of the wave functions ψ_{v_1}, $\psi_{v_2 l}$, ψ_{v_3} that the non-vanishing elements of V_1 are those in which (*i*) v_1 and v_1' may differ by any integer, (*ii*) v_2 and v_2' differ by an even integer, (*iii*) v_3 and v_3' differ by an even integer, and (*iv*) $l'=l$. Hence the perturbed wave functions (89) possess the same evenness and oddness in the coordinates r and z and depend in the same way on φ (*i.e.*, through the same factor $e^{\pm il\varphi}$) as the wave function of the unperturbed system.

From (48) of Chap. II, one obtains the components of the electric moment due to the vibrations of the molecule along and perpendicular to the axis of the molecule,

$$\mathfrak{M}_z = \left(\frac{\partial \mathfrak{M}_z}{\partial z}\right)_0 z , \qquad \mathfrak{M}_x \pm i\,\mathfrak{M}_y = \left(\frac{\partial \mathfrak{M}_r}{\partial r}\right)_0 \cdot r e^{\pm i\varphi} \tag{90}$$

By means of the properties of the wave functions of the perturbed system shown above, the following results can readily be established:

$$\mathfrak{M}_z(v;v') = \int \overset{*}{\Psi}_v \, \mathfrak{M}_z \, \Psi_{v'} \, d\tau = 0 \text{ unless } l'=l,\ v'_2-v_2=\text{even},\ v'_3-v_3=\text{odd},$$

$$(\mathfrak{M}_x \pm i\,\mathfrak{M}_y)\,(v;v') = \int \overset{*}{\Psi}_v \, (\mathfrak{M}_x \pm i\,\mathfrak{M}_y) \Psi_{v'} \, d\tau = 0 \text{ unless } l'=l\pm 1,$$

$$v'_2-v_2=\text{odd},\ v'_3-v_3=\text{ even}. \tag{91}$$

From these, the selection rules follow:

(i) For transitions which are accompanied by changes of the electric moment along the axis ($\mathfrak{M}_z \neq 0$),

---

[2] The ten relations in (87) are not sufficient for the calculation of the 9 constants and the 3 frequencies ω's. Additional relations are furnished by the convergence factor of the rotational lines. See Adel and Dennison, Phys. Rev. 44, 99, (1933), also Chapter IV, §4, A.

$$\Delta l = 0, \qquad \Delta v_2 = \text{even}, \qquad \Delta v_3 = \text{odd} \tag{92a}$$

(ii) For transitions which are accompanied by changes of the electric moment in directions perpendicular to the axis ($\mathfrak{M}_x \pm i\mathfrak{M}_y \neq 0$),

$$\Delta l = \pm 1, \quad \Delta v_2 = \text{odd}, \qquad \Delta v_3 = \text{even}. \tag{92b}$$

In the Raman effect, it has been shown in §6, equs. (51) of Chap. II. that of all the coefficients $\left(\frac{\partial \alpha_{ij}}{\partial X_k}\right)_0$, only $\left(\frac{\partial \alpha_{ii}}{\partial q}\right)_0$, $i=x, y, z$ do not vanish. The selection rules are then obtained by considering the matrix elements of $\left(\frac{\partial \alpha_{ii}}{\partial q}\right)_0 q$, $i=x, y, z$. In a first approximation in which the vibrations are regarded as simple harmonic, one readily obtains

$$\Delta v_1 = \pm 1, \quad \Delta v_2 = \Delta v_3 = \Delta l = 0. \tag{93}$$

In the next approximation in which the anharmonicity of the vibrations is taken into account, it is necessary to find the matrix elements of $\left(\frac{\partial \alpha_{ii}}{\partial q}\right)_0 q$ with respect to the wave functions (89) of the perturbed system. Since the change of the polarizability $\left(\frac{\partial \alpha_{ii}}{\partial q}\right)_0 q$ is independent of the normal coordinates of the vibrations ν_2 and ν_3, and from what has been said of the properties of the wave functions (89), one readily obtains the following selection rules

$$\Delta v_1 = \text{arbitrary}, \quad \Delta v_2 = \text{even}, \quad \Delta v_3 = \text{even}, \quad \Delta l = 0. \tag{93a}$$

It follows from these and (92a), (92b) that combination frequencies that are active in absorption ($\Delta v_2 + \Delta v_3 = \text{odd}$) are not active in the Raman effect, while those that are active in the Raman effect ($\Delta v_2 + \Delta v_3 = \text{even}$) are not active in absorption.

The above results, namely that only harmonics $\Delta v = \text{even}$ of antisymmetrical vibrations are active in the Raman effect, is perfectly general for all molecules possessing a center of symmetry. Consider a vibration ν_i which is antisymmetrical with respect to the center. As the change in the polarizability is a tensor and is hence an even function in the normal coordinate X_i, so must be the induced electric moment. Hence the matrix elements of $\mathfrak{M}_x$, say,

$$\mathfrak{M}_x(v; v') = \int \overset{*}{\Psi}_{v_i} \mathfrak{M}_x \Psi_{v_i'} \, dX_i$$

do not vanish only when $\overset{*}{\Psi}_{v_i} \Psi_{v_i'}$ is even, *i.e.*, $\Delta v = \text{even}$.

Perturbation calculations of the energies have been carried out for the linear X-Y-Z molecule by Adel[2]; for the triangular YX_2 molecule by Bonner[3]; and for the the linear symmetrical Y_2X_2 molecule by Wu and Kiang[4]. We shall refer to these papers for the energy expressions. But as another illustration of the consequence of the symmetry properties of the vibrations on the selection rules, we shall discuss the case of the YX_2 molecule below.

It has been shown in §6, equ. (49), Chap. II that the vibrations $\boldsymbol{\nu}_1$ and $\boldsymbol{\nu}_2$ are accompanied by changes of the electric moment along the symmetry axis and $\boldsymbol{\nu}_3$ perpendicular to the symmetry axis. To obtain the selection rules for the harmonic and the combination bands, we have to find the matrix elements of the electric moment of the perturbed system (*i.e.*, by anharmonicities). The wave functions $\Psi v_1v_2v_3$ of the perturbed system are given by (89) in which the anharmonic potential V_1 must be an even function of the coordinate x in Fig. 4, and by equations (28) of Chap. II, V_1 must be even in the coordinate X_3. On account of the properties (7) of the unperturbed wave functions $\psi \overset{\circ}{v}_1$, $\psi \overset{\circ}{v}_2$, $\psi \overset{\circ}{v}_3$, it follows that in the expression (89), v_1' and v_2' may be entirely arbitrary, but v_3' must be such that the difference $|v_3-v_3'|$ is an even integer. Hence the wave function of the perturbed system in the state v_1, v_2, v_3 is even in the normal coordinate X_3 for v_3 even, and odd in X_3 for v_3 odd, just as the wave function $\psi \overset{\circ}{v}_1$, $\psi \overset{\circ}{v}_2$, ψv_3 of the unperturbed system.

We are now in a position to obtain the selection rules. The matrix elements of the change of the electric moment along the symmetry axis (Fig. 8) are given by

$$\mathfrak{M}_z (v_1\, v,\, v_3;\, v_1'\, v_2'\, v_3') = \int \overset{*}{\Psi}_{v_1 v_2 v_3}\, \mathfrak{M}_x\, \psi_{v'_1 v'_2 v_3'}\, d\tau.$$

Since $\mathfrak{M}_z$ is independent of X_3, it follows from what has just been said of the perturbed wave functions that v_3-v_3' must be an even integer for the matrix element not to vanish. The matrix elements of the change of the electric moment perpendicular to the symmetry axis are given by

$$\mathfrak{M}_x (v_1\, v_2\, v_3;\, v_1'\, v_2'\, v_3') = \int \overset{*}{\psi}_{v_1 v_2 v_3}\, \mathfrak{M}_x\, \psi_{v_1' v_2' v_3'}\, d\tau.$$

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[2] A. Adel, Phys. Rev. 46, 222, (1934). The expressions for the coefficients x_{ij}'s contain a few errors which obviously have the same origin as those in the paper on CO_2. See footnote (1).

[3] L. G. Bonner, Phys. Rev. 46, 458, (1934).

[4] T. Y. Wu and A. T. Kiang, Jour. Chem. Phys. 7, 178, (1939).

As $\mathfrak{M}_x$ is independent of X_1 and X_2, but is an odd function of X_3, it follows that the matrix elements do not vanish only when $v_3 - v_3'$ is odd. Hence the following selection rules are obtained:

(i) For transitions accompanied by changes of the electric moment parallel to the symmetry axis,

$$\Delta v_1, \Delta v_2 \quad \text{arbitrary,} \qquad \Delta v_3 = \text{even.} \tag{94a}$$

(ii) For transitions accompanied by changes of the electric moment perpendicular to the symmetry axis,

$$\Delta v_1, \Delta v_2 \quad \text{arbitrary,} \qquad \Delta v_3 = \text{odd} \tag{94b}$$

It will be seen that these rules are satisfied by the spectrum of the water molecule (Chap. V).

The selection rules for the linear symmetrical Y_2X_2 molecule have been obtained by Dennison[5] on similar considerations. They are:

(i) For the change of the electric moment || to the axis of the molecule,

$$|\Delta l_4| = |\Delta l_5|, \qquad \text{and either} \begin{cases}\Delta v_3 \text{ odd} \\ \Delta v_4 \text{ even} \\ \Delta v_5 \text{ even}\end{cases} \text{or} \begin{cases}\Delta v_3 \text{ even} \\ \Delta v_4 \text{ odd} \\ \Delta v_5 \text{ odd}\end{cases} \tag{95a}$$

(ii) For the change of the electric moment ⊥ to the axis of the molecule,

$$|\Delta l_4| = |\Delta l_5| \pm 1, \quad \text{and either} \begin{cases}\Delta v_3 \text{ even} \\ \Delta v_4 \text{ odd} \\ \Delta v_5 \text{ even}\end{cases} \text{or} \begin{cases}\Delta v_3 \text{ odd} \\ \Delta v_4 \text{ even} \\ \Delta v_5 \text{ odd}\end{cases} \tag{95b}$$

In both cases, Δv_1 and Δv_2 may be arbitrary. The meaning of the quantum numbers and the modes of vibrations will be given in Chap. V.

B) Mecke's method

A different approach to the problem of the anharmonic vibrations of a complex molecule has been recently suggested by Mecke[1]. Instead of the normal coordinates, the Schroedinger equation is expressed in terms of the relative displacements in the different valence bonds and hence contains cross terms of the form $\frac{\partial}{\partial q_1} \frac{\partial}{\partial q_2}$. For example, with two valence bonds, or more generally, two oscillators, the Schroedinger equation can be written in the form

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[5] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931); The same results are obtained by the method of the group theory by Tisza, Zeits. f. Physik 82, 48, (1933).

[1] R. Mecke, Zeits. f. Physik 99, 217, (1936); R. Mecke and R. Ziegler, Zeits. f. Physik 101, 405, (1936).

$$\left\{\frac{1}{\mu_1}\frac{\partial^2}{\partial q_1^2}+\frac{2\alpha}{\sqrt{\mu_1\mu_2}}\frac{\partial^2}{\partial q_1\partial q_2}+\frac{1}{\mu_2}\frac{\partial^2}{\partial q_2^2}+\frac{8\pi^2}{h^2}[E-V_1(q_1)-V_2(q_2)\right.$$
$$\left.-2V(q_1,q_2)\,]\right\}\psi=0, \tag{96}$$

in which α is a parameter depending on the masses and the positions of the atoms forming the two oscillators and measures the coupling between them. Equation (96) is then separated by neglecting the terms in $\frac{\partial^2}{\partial q_1\partial q_2}$ and $V(q_1, q_2)$ which are later treated as perturbations. For each individual oscillator, one can start with a better approximation than the harmonic oscillator by employing for example the Morse potential (25). The energy of the uncoupled system is, according to (31a),

$$E_{mn}/h=(m+\tfrac{1}{2})\,\nu_1-x_1\,\nu_1\,(m+\tfrac{1}{2})^2+(n+\tfrac{1}{2})\,\nu_2-x_2\nu_2(n+\tfrac{1}{2})^2. \tag{97}$$

The effect of the coupling between the two oscillators can now be obtained by calculating the perturbations. Consider first the mechanical coupling. It can be shown that the diagonal matrix elements of the perturbation $\frac{\partial^2}{\partial q_1\partial q_2}$ vanish, *i.e.*,

$$\iint \overset{*}{\psi}_m(q_1)\cdot\overset{*}{\psi}_n(q_2)\,\frac{d\psi_m(q_1)}{dq_1}\cdot\frac{d\psi_n(q_2)}{dq_2}\cdot dq_1dq_2=0, \tag{98}$$

and the non-vanishing elements have the property

$$\int\psi_m\frac{d\psi_n}{dq}\cdot dq=-\int\psi_n\frac{d\psi_m}{dq}\cdot dq. \tag{99}$$

Thus in general the mechanical coupling contributes only to a second order energy change (*i.e.*, proportional to α^2). Integrals of the form (99) can be evaluated by means of the relations (31)—(38). The results are as follows:

$$\int\psi_0\,d\psi_1=-\tfrac{1}{2}\sqrt{\frac{8\pi^2\mu}{h}}\;\sqrt{(1-3x)\,\nu}\;;$$

$$\int\psi_1\,d\psi_2=-\tfrac{1}{2}\sqrt{\frac{8\pi^2\mu}{h}}\;\sqrt{\frac{2(1-3x)(1-5x)\nu}{(1-2x)}}$$

$$\int\psi_{n-1}d\psi_n\simeq-\tfrac{1}{2}\sqrt{\frac{8\pi^2\mu}{h}}\;\sqrt{n(1-3nx)\,\nu}, \tag{100}$$

since $x=h\nu/4D$ is small. Similarly, one finds

$$\int \psi_0 \, d\psi_2 = -\tfrac{1}{2}\sqrt{\frac{8\pi^2\mu}{h}} \sqrt{\frac{2(1-5x)}{(1-2x)}}\, x\,\nu;$$

$$\int \psi_{n-2} d\psi_n \simeq -\tfrac{1}{2}\sqrt{\frac{8\pi^2\mu}{h}} \sqrt{n(n-1)}\,x\nu$$

$$\int \psi_0 \, d\psi_3 = -\tfrac{1}{2}\sqrt{\frac{8\pi^2\mu}{h}}\, x\sqrt{\frac{6(1-7x)\nu}{(1-2x)(1-3x)}}\,. \tag{101}$$

It is seen that the integral $\int \psi_m \, d\psi_n$ contains a factor $(x)^k$ where $2k = |m-n| - 1$. As x is small, one needs only consider, for practical purposes, the elements $H'(m, n;\ m\pm 1,\ n\mp 1)$.

An interesting application of this method is perhaps in the case of two identical anharmonic oscillators, each of frequency ν, coupled together. If the coupling be strong, one must calculate the change in the fundamental frequencies as the result of the coupling. Denoting the two oscillators by a and b, we have then a resonance between the two states $\psi_0(a) \cdot \psi_1(b)$ and $\psi_1(a) \cdot \psi_0(b)$; that is, the excitation of either oscillator to the first vibrational state corresponds to the same energy. The energy changes due to this resonance are given according to the perturbation theory for degenerate systems by the secular equation

$$\begin{vmatrix} H'(1,0;1,0) - E' & H'(1,0;0,1) \\ H'(0,1;1,0) & H'(0,1;0,1) - E' \end{vmatrix} = 0, \tag{102}$$

where

$$H'(1,0;0,1) = \frac{2\alpha h^2}{8\pi^2\mu}\int \psi_1(a)\frac{d\psi_0(a)}{da}\,d\,a \int \psi_0(b)\,\frac{d\psi_1(b)}{db}\,db \quad \text{etc.,} \tag{103}$$

From (98), (99) and (100), one obtains

$$E' = \pm\tfrac{1}{2}\,\alpha h\nu\,(1-3x) \simeq \pm\tfrac{1}{2}\,\alpha h\nu\,, \tag{104}$$

Thus as the result of the coupling, the fundamental frequencies of the oscillators become $\nu + \frac{1}{2}\alpha\nu$ and $\nu - \frac{1}{2}\alpha\nu$. Substitution into (97) gives

$$E/h = \nu(v+1) + \tfrac{1}{2}\,\alpha l\nu - \tfrac{1}{2}\,x\,\nu\left[(v+1)^2 + l^2\right] + \text{terms in } \alpha x, \tag{105}$$

where

$$v = m + n, \qquad l = m - n. \tag{106}$$

When the coupling is loose, the energy change comes in general in the second order. Neglecting the interactions between such states as

v, l (m, n) and v, $l\pm 4$ $(m\pm 2, n\mp 2)$, one obtains from (16) by means of (100) the following result

$$\begin{aligned} E'' &= -x\nu\left[1+\frac{(v+1)^2}{l^2-1}\right]\left[1-3(v+1)x\right]\left(\frac{\alpha}{4x}\right)^2 \\ &\simeq -x\nu\left[1+\frac{(v+1)^2}{l^2-1}\right]\left[\frac{\alpha}{4x}\right]^2. \end{aligned} \tag{107}$$

When $l=\pm 1$, the states n, $n\mp 1$ and $n\mp 1$, n are degenerate, and the second order energy can be shown to be

$$E''_{v,1} = x\nu(v-1)(v+3)\left(\frac{\alpha}{8x}\right)^2, \tag{108}$$

while the first order energy of the resonating states is given by the secular equation

$$\begin{vmatrix} H'(n+1,n;n+1,n)-E' & H'(n+1,n;n,n+1) \\ H'(n,n+1;n+1,n) & H'(n,n+1;n,n+1)-E' \end{vmatrix} = 0 \tag{109}$$

or

$$E' = \pm\tfrac{1}{4}\alpha h\nu(v+1). \tag{109a}$$

The energy expression is therefore

$$E/h = \begin{cases} (v+1)\nu - \frac{1}{2}x\nu\left[(v+1)^2+l^2\right] - x\nu\left[1+\frac{(v+1)^2}{l^2-1}\right]\left(\frac{\alpha}{4x}\right)^2, & l\neq\pm 1 \\ (v+1)\nu - \frac{1}{2}x\nu\left[(v+1)^2+l^2\right] \pm \frac{1}{4}\alpha\nu(v+1) + \\ \qquad x\nu(v-1)(v+3)\left(\frac{\alpha}{8x}\right)^2, & l=\pm 1. \end{cases} \tag{110}$$

For intermediate couplings, the theory of perturbation shows that the energy is of the form

$$E/h = \nu(v+1) + A\alpha + Bx, \tag{111}$$

where the coefficients A and B are functions of the quantum numbers v and l, and for any given state v, l can be determined from the coefficients in the two extreme cases (105) and (110). For this correlation, it is necessary to consider the symmetry properties of the states v, l. We shall not go into this but refer to the papers of Mecke for details and applications.

This method of Mecke differs from the normal coordinate method chiefly in the order in which the approximations are made. One starts with a system of independent anharmonic oscillators and treats the mechanical and electrical couplings between them as perturbations; while in the normal coordinate method the mechanical coupling and part of the electrical coupling are included in the initial approximation but the anharmonicity is treated as a perturbation. In systems in which the couplings are loose and the anharmonicities pronounced, this method may be expected to form a better approximation than the normal coordinate method. Since, however, one has to neglect terms like $V(q_1, q_2)$ because of the difficulty in their evaluation, one would hardly expect to obtain very good results with this method except in extreme cases.[2]

§4. **Resonance in Vibrational Energy Levels**

In the wave mechanical treatment of the vibrations of molecules in §2, it has been tacitly assumed that the system is non-degenerate, *i.e.*, to each energy level there corresponds one independent wave function. (The case of the degeneracy due to the isotropy of motion in a plane has been treated in §1, C. It is shown there that the degeneracy can be partly removed by introducing suitable perturbations). In this section we shall discuss two important cases of resonance degeneracy in the theory of the vibrational spectra of molecules.

A) Resonance due to Identical Potential Minima

When an atom (or a group of atoms) in a molecule has more than one positions of equilibrium which are physically indistinquishable from one another, there is a splitting of certain energy levels as the result of the interactions between the resonating levels. We shall give the wave mechanical theory of two cases of such resonance effects.

(*i*) One-dimensional two-minimum problem

This is suggested by the observed experimental fact that certain bands of the ammonia molecule are doubled[1]. We shall show that the wave mechanical treatment of the problem offers an explanation of this doubling.

Consider any one of the two parallel vibrations ν_1 and ν_3 of the pyramidal YX_3 molecule, in which the Y atom moves along the axis of symmetry of the molecule, about a position of equilibrium at a distance x_0 from the plane of the X atoms. The potential energy as a function of the distance between the Y atom and the plane of the X atoms would be given by a curve of the general form shown in Fig. 10. Since the situation is symmetrical with respect to the plane of the X atoms, the

[2] See Chap. V, §2, A on C_2H_2.

[1] See Chap. V, §2, B on NH_3.

potential energy would be given by a curve of the form in Fig. 12. The problem now is to find the energy of vibration in this potential field possessing two exactly identical valleys.

The Schroedinger equation for the system can be written in the form

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}\Big[E - V(x)\Big]\psi = 0, \qquad (112)$$

where μ is a function of the masses of the Y and X atoms[2]. The solution of this equation depends on a knowledge of the form of the potential $V(x)$. If the two potential valleys are separated by a "hill" of infinite extent, then the Y atom moving in one region would behave as if the other valley were non-existent. In this case the energy would be given, to a first approximation, by[3]

$$\frac{2\pi}{h}\int_{x_1}^{x_2} P\,dx = (n + \tfrac{1}{2})\,\pi, \qquad (113)$$

where

$$P^2 = 2\mu\,|\,E - V(x)\,| \qquad (114)$$

Corresponding to each value of the quantum number n, there is one wave function $\psi(x)$ which is simply the orthogonal Hermitian function (10) if the potential is quadratic in $(x - x_0)$, or the function (27) if the potential is of the form (25). If the potential hill between the two valleys is finite, then according to the quantum mechanics the Y atom moving initially in one region has a small but finite probability of going through the potential hill into the other region. This is obviously not allowed in the classical theory but is a characteristic result of the quantum mechanics, the mathematical statement of which is briefly as follows.

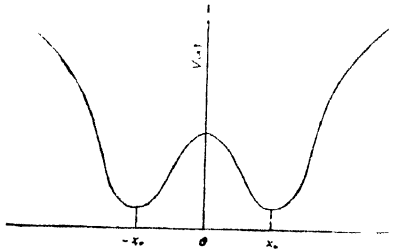

Fig. 12. Potential field having two minima

One has now to find the eigenvalues of the equation (112) with the potential in Fig. 12. The boundary conditions on the solutions are that they must vanish at $x=-\infty$ and $x=\infty$. For each value of the quantum number n, one finds two solutions one of which is symmetrical with respect to a reflection on the plane of the X atoms (an operation which is brought about by the interchange of two of the X atoms), *i.e.*, is an even function of the coordinate x; the other is antisymmetrical with respect to this reflection, or, it is an odd function of x. Corresponding to these two wave functions, there are now two eigenvalues which are given, to the same approximation as in (113), by the equation[4]

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[2] Here μ is not the reduced mass of the Y and the 3 X atoms since really one has to deal with two parallel vibrations. See Chap. V, equ. (70a).

[3] This is obtained by the so-called Wentzel-Kramers-Brillouin method of solving the Schroedinger equation. For a discussion of this method, see for example Uhlenbeck and Young, Phys. Rev. 36, 1150, (1930) and R. E. Langer, Phys. Rev. 51, 669, (1937) and the references given in these papers.

$$\frac{2\pi}{h}\int_{x_1}^{x_2} P\,dx = (n+\tfrac{1}{2})\,\pi \pm \delta, \qquad (115)$$

where

$$\delta = tan^{-1}\left(\frac{1}{2\alpha^2}\right) \qquad \alpha^2 = exp\left(\frac{2\pi}{h}\int_{-x_1}^{x_1} P\,dx\right) \qquad (116)$$

and P has the same meaning as in (114). Equation (115) shows that the quantum mechanical effect of the resonance between the two levels in the two valleys given by (113) is to split the level into two. The splitting separation depends on the area under the potential hill through the expressions in (116). The antisymmetrical wave function corresponds to the higher one, and the symmetrical wave function to the lower one of the two levels given by (115). When the potential hill is very high so that δ is small, it will be found from (115) that the splitting of the level is symmetrical with respect to the position given by (113).

Perhaps it is well to consider the splitting of the energy levels in the light of the uncertainty principle. Since it is the square of the wave function that determines the probability of finding the Y atom at a distance x from the plane of the X atoms, it is clear that both the symmetrical and the antisymmetrical wave functions give the same probability for finding the Y atom at the distance x on both sides of the plane of the X atoms. This is equivalent to saying that when the energy of the system is known to be either one of the two values given by (115), then it is as likely to find the Y atom on one side of the plane of X atoms as on the other. In other words, it is not possible to say definitely on which side of the plane will the Y atom be found. If one forms linear combinations of the two wave functions such as $\frac{1}{\sqrt{2}}(\psi_{sym.}+\psi_{anti})$ and $\frac{1}{\sqrt{2}}(\psi_{sym}-\psi_{anti})$, so that now their squares do not vanish on only one side of the X_3 plane and hence the Y atom is known to be definitely on that side, the energy of the system becomes in both cases E_i, the value given by (113), and hence is undetermined by the amount Δ_i, the splitting separation between the two levels given by (115). Since physically neither side of the X_3 plane is to be preferred to the other, the correct description of the situation must be given by the wave functions ψ_{sym} and ψ_{anti} instead of their combinations above.

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[4] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. 41, 313, (1932); also T. Y. Wu, Phys. Rev. 44, 727, (1933). See footnotes below.

To obtain the two energy levels corresponding to the two wave functions ψ_{sym} and ψ_{anti}, one has to know the form of the potential $V(x)$. When one is considering the low vibrational states, one may in a first approximation represent those parts of the $V(x)$ curve near the minima by parabolas. The splitting of the energy level depends on the potential $V(x)$ only through the integrals $\int P\,dx$ in (115) and (116) in a first approximation, but is insensitive to changes in the exact form of the potential curve provided the values of the integrals $\int P\,dx$ remain unchanged. Hence one may, also as an approximation, join the two parabolic curves by a simple sine curve, or even by a straight line[5]. The eigenvalues given by (115) can then be expressed in terms of the value E_i given by (113) and the parameters defining the potential curve and entering here though (116). For splittings that are small, one finds

$$\left.\begin{matrix} E_i\,(\text{anti}) \\ \\ E_i\,(\text{sym}) \end{matrix}\right\} = E_i \pm \tfrac{1}{2}\Delta_i. \qquad (117)$$

Let us now consider the selection rules for the transitions between two states with quantum numbers n_1 and n_2, and let their splitting separations be Δ_1 and Δ_2 respectively. It follows from (116) that $\Delta_2 > \Delta_1$ if $n_2 > n_1$. The electric moment along the axis of the molecule is evidently proportional to the coordinate x. The matrix elements of the electric moment do not vanish for transitions between levels with opposite symmetry properties, for the integral

$$\mathfrak{M}_x\,(n_2, n_1) = \int_{-\infty}^{\infty} \overset{*}{\psi}_{n_2}\, x\, \psi_{n_1}\, dx \qquad (118)$$

does not vanish if the wave functions ψ_{n_1}, ψ_{n_2} are of opposite symmetry character, but vanishes when they are of the same symmetry character,

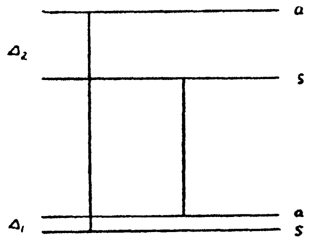

Fig. 13. Energy levels of two-minimum problem

since the integrand is an even and an odd function of x in the two cases respectively. Thus instead of one single transition, there are now two possible transitions, giving rise to a doubling of the band. The separation between the two component bands is equal to the sum $\Delta_1 + \Delta_2$ of the splitting separations of the two states involved, as shown in Fig. 13. The Raman lines, however, arise from transitions between levels of the same symmetry character.

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[5] P. M. Morse and E. C. G. Stueckelberg, Helv. Phys. Acta 4, 337, (1931); D. M. Dennison and G. E. Uhlenbeck, loc. cit.; Exact solutions of (112) for some special forms of V(x) are given by Morse and N. Rosen, Phys. Rev. 42, 210, (1932); M. F. Manning, Jour. Chem. Phys. 3, 136, (1935); also F. T. Wall and G. Glockler, Jour. Chem. Phys. 5, 314, (1937).

From the observed doubling separations $\Delta_i + \Delta_j$, it is possible to calculate approximately the values of such quantities as the distance x_0, *i.e.*, the height of the pyramid in the position of equilibrium, and the height of the potential hill. Application of the theory to the ammonia molecule NH_3 will be taken up in Chap. V.

(*ii*) Torsional oscillation (Identical potential minima)

In molecules of the ethane type, one of the degrees of freedom is a torsional oscillation or rotation of the two CH_3 groups with respect to each other about the carbon-carbon single bond. The vibrational and the rotational parts of the wave function of the molecule can be shown, in a first approximation, to be

$$\Psi = \Pi\, \psi_{v_i} \cdot e^{iM\psi}\, e^{iK\varphi}\, \Theta(\cos\vartheta) \cdot \psi(\gamma), \tag{119}$$

where the ψ_{v_i}'s are the wave functions corresponding to the various normal vibrations, $e^{iM\psi}\ e^{ik\varphi}\ \Theta\ (\cos\theta)$ is the rotational wave function for the molecule regarded as rigid rotator and is given by (18) of Chap. IV, and $\psi\ (\gamma)$ is the wave function for the torsional degree of freedom. This last wave function is the solution of the Schrödinger equation

$$\frac{d^2\psi}{d\gamma^2} + \frac{4\pi^2 I}{h^2}\,[E - V(\gamma)]\,\psi = 0 \tag{120}$$

where $V(\gamma)$ is the potential energy of the two CH_3 groups and is a periodic function of the angle γ defining the relative orientation of the two groups, namely,

$$V\ (\gamma) = V\left(\gamma + \frac{2\pi}{3}\right), \tag{121}$$

and I is the moment of inertia of each CH_3 group about the axis of symmetry. The equation (121) is to be solved subject to periodicity conditions to be obtained as follows: The wave function (119) must remain unchanged on rotating either CH_3 group through 2π with respect to the other group. This change in the angle γ changes the Euler's angle φ defining the orientation of the C_2H_6 molecule as a whole in Fig. 16 and equ. (18) of Chap. IV by π[1]. Hence the conditions are as follows:

$$\begin{aligned} \psi(\gamma) &= \psi(\gamma+2\pi) \qquad \text{for } K = \text{even},\\ \psi(\gamma) &= -\psi(\gamma+2\pi) \qquad \text{for } K = \text{odd}. \end{aligned} \tag{122}$$

The eigen values of (120) are then the energies of this degree of freedom.[2] [3]

While the exact arrangement of the energy levels of (120) can not be determined without a knowledge of the exact form of the potential $V(\gamma)$, the following qualitative remarks can be made on quite general considerations. When the potential valleys of $V(\gamma)$ in Fig. 14 are separated by infinite potential hills, the motion is then one of pure oscillatory motion of the two groups about the position of equilibrium. When the potential hills are of finite height, however, the resonance between the energy levels in the different identical regions of possible motion gives rise to a splitting of the energy levels given by (113), the situation being similar to the case discussed under (*i*) for the YX_3 molecule above. In the case of the C_2H_4 type molecules, each level is split into four, of which two levels remain degenerate. In the case of the

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[1] The Euler's angle φ for the molecule as a whole is defined as $\frac{1}{2}(\gamma_1+\gamma_2)$ where γ_1 and γ_2 are the Euler's angles for the two CH_3 groups so that $\gamma=\gamma_2-\gamma_1$.

[2] The symmetry properties of the wave functions of the individual levels must further include the spin wave functions due to the nuclear spins of the six H atoms in the case of the ethane molecule. Due to the spin ½ for the H atomic nucleus, there are $2^6=64$ spin orientations. It can be shown that these 64 wave functions divide themselves into 6 non-combining classes with different symmetry properties with respect to the symmetry operations for the molecule. These classes have the following statistical weights: 32, 8, 6, 2, 10, 6. Considerations of the symmetry properties of these wave functions are important for the calculations of the contribution of this degree of freedom to such quantities as the entropy, free energy and molecular heat at very low temperatures. See E. Teller and K. Weigert, Gött. Nachr. 2, 218, (1933); K. Schäfer, Zeits. f. phys. Chem. B 40, 357, (1938); E. B. Wilson, Jr. Jour. Chem. Phys. 6, 740, (1938), for detailed discussions of the group-theory method of studying the symmetry classes and the calculations of the thermodynamic quantities.

[3] For the ethylene type molecules in which the two groups under consideration are joined by a double bond, the Schrödinger equation is the same as (120), except that now the potential $V(\gamma)$ is determined mainly by the directional properties of the bonds between the two carbon atoms, while in C_2H_6 the potential arises from the interactions between the H atoms in the two CH_3 groups and possibly also from the interactions between the H atoms of one CH_3 group with the C-H bonds in the other group. For ethylene, the potential is such that the motion is one of oscillation, as shown by specific heat data for the molecule (see Chap. V, section on C_2H_4).

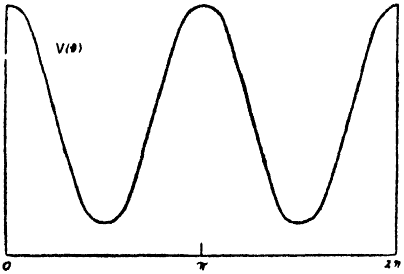

Fig. 14a. Periodic potential in C_2H_4 type molecule

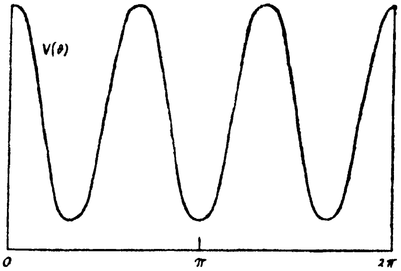

Fig. 14b. Periodic potential in C_2H_6 type molecule

C_2H_6 type molecules, each level is split into six of which there are two coincident pairs. The total number of levels and the degeneracy unremoved by taking into account the possibility of going through the potential hills are determined by the symmetry of the potential field $V(\gamma)$, but are not dependent on the method of solving the equation (120). The splitting separations of the levels again depend on the value of the integral $\int P\, d\gamma$ taken over the region under the potential hill, as in (116). They increase as the height of the potential hills decrease, or, for a fixed potential function, they increase as one goes up to higher energy levels. In the limit when the potential function is a constant independent of the angle γ, the oscillation passes over into a uniform rotational motion of the two groups about the symmetry axis. The connection between the energy levels in the limit of pure rotation and in the limit of pure oscillation is shown schemetically in Figs. 15a and 15b.

In the figures, the doubly degenerate levels are drawn slightly apart for the sake of clearness. The numerical values of the energy levels and their splittings in a given molecule must be obtained from equation (120). In the absence of any accurate knowledge concerning the forms of the potential $V(\gamma)$, we may as an approximation represent $V(\gamma)$ by a simple periodic function like $A \cos 2\gamma$ for the C_2H_4 type molecules and $A \cos 3\gamma$ for the C_2H_6 type molecules, where A is a parameter giving the height of the potential hills. With such a form for $V(\gamma)$, the eigenvalues of the Schrödinger equation (120) can be obtained either from the standard solutions of the Mathieu equation, or by a perturbation method. Reference must be made to the work of Nielsen and Koenig for further details[4].

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[4] H. H. Nielsen, Phys. Rev. 40, 445, (1932); H. D. Koenig, Phys. Rev. 44, 675, (1933).

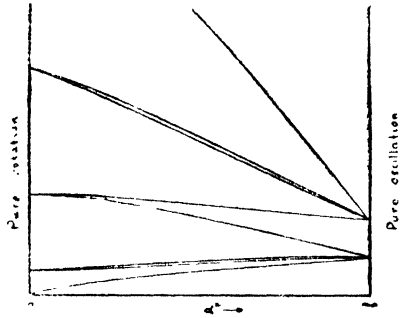

Fig. 15a. Energy levels of torsional degree of freedom in C_2H_4 type molecule

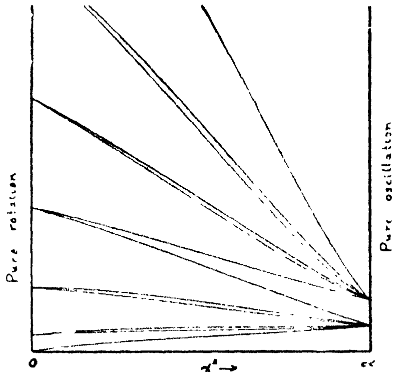

Fig. 15b. Energy levels of torsional degree of freedom in C_2H_6 type molecule

A special case of the C_2H_4 type molecules is suggested by such molecules as the *cis* and the *trans* dichlorethylenes $C_2H_2Cl_2$.[5] The potential $V(\gamma)$ in such cases is periodic in 2π and the potential valleys are different in shape and depth, corresponding to the two stable forms of the isomers. In this case, the remaining degeneracy of the levels in the C_2H_4 type molecules (Fig. 15a) is completely removed by a further splitting of the double levels.

B) Accidental Degeneracy

In some molecules it may happen that two normal frequencies, or one fundamental and the harmonic of a second fundamental, are coincident or very close to each other. Under certain proper condition as to the symmetry properties of the two levels, their interactions will result in a mutual sharing of their properties, or in the language of the wave mechanics, in a mixing of their wave functions. The method for treating such accidental degeneracies is the method of the perturbation theory for degenerate systems.

The first example of such degeneracy is the vibration ν_1 and the harmonic $2\nu_2$ of the carbon dioxide molecule. We have seen in §6, Chap. II, that ν_1 is the only Raman effect active vibration of a linear symmetrical YX_2 molecule of which considerable amount of data shows the CO_2 molecule to be an example.[1] The Raman spectrum shows, however, that there are two lines quite close together in the position of ν_1. Their intensities are such that they are incompatible with the assumption that one of the lines may be the harmonic of the fundamental ν_2. Fermi[2] first suggested that this is due to a resonance between ν_1 and $2\nu_2$. The theory has been further worked out by Dennison and Adel[3] who showed that on this theory and by taking into account second order perturbations as done in §3, A, a completely satisfactory interpretation of the entire spectrum of the melecule can be obtained.

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[5] T. Y. Wu, Phys. Rev. 45, 66, (1934).

[1] For the experimental data and their interpretations, see Chap. V.

We shall in the initial approximation assume that $\omega_1 = 2\omega_2$, and in the next (first) approximation $\omega_1 = 2\omega_2 + \Delta$, where Δ is small. On substituting this into the expressions (80a) for the kinetic and the potential energy, one has, in the zeroth approximation,

$$H^\circ = \frac{2\pi^2}{h}\left[2\omega_2 p^2_\sigma + \omega_3 p_\xi^2 + \omega_2 p_\varrho^2 + \frac{\omega_2}{\varrho^2} p_\varphi^2\right] + \frac{h}{2}\left[2\omega_2\sigma^2 + \omega_2\varrho^2 + \omega_3\xi^2\right], \tag{123}$$

and in the first and the second approximations, on combining with (83) and (84),

$$H' = \frac{2\pi^2}{h}\Delta p_\sigma^2 + \frac{h\Delta}{2}\sigma^2 + h\left[a\sigma^3 + b\sigma\varrho^2 + c\sigma\xi^2\right] \tag{124}$$

$$H'' = h\left[d\sigma^4 + e\varrho^4 + f\xi^4 + g\sigma^2\varrho^2 + i\varrho^2\xi^2 + j\sigma^2\xi^2\right]. \tag{125}$$

The zeroth order energy (82) now becomes

$$E^\circ = h\left[2\,\omega_2(v_1 + \tfrac{1}{2}) + \omega_2(v_2 + 1) + \omega_3\,(v_3 + \tfrac{1}{2})\right]. \tag{126}$$

The system is now degenerate in two respects: (1) the energy E° is independent of l, and (2) E° depends on the quantum numbers v_1 and v_2 only through the sum $2v_1 + v_2$, but not on the individual values of v_1 and v_2. We are at present not interested in the degeneracy in l, which has been treated in §1, C and again in §3, A. We are chiefly concerned with the degeneracy in ν_1 and $2\nu_2$. This degeneracy can be removed by taking into consideration the interaction between the two vibrations. For this purpose, we need only consider that part of the perturbation potential (110) which is a function of the normal coordinates σ and ϱ of the two vibrations ν_1 and ν_2 alone, namely,

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[2] E. Fermi, Zeits. f. Physik 71, 250, (1931).

[3] D. M. Dennison, Phys. Rev. 41, 304, (1932); A. Adel and D. M. Dennison, Phys. Rev. 43, 716, (1933).

$$H_1' = \frac{2\pi^2 \Delta}{h} p_\sigma^2 + \frac{h\Delta}{2} \sigma^2 + hb\sigma\varrho^2. \tag{127}$$

For the degenerate states corresponding to a certain value of the sum $2v_1+v_2$, the first order energy changes due to H_1' in (113) are given by the secular equation

$$\left\| H_1' \, (v_1, v_2; v_1', v_2') - E' \, \delta \, (v_1, v_2; v_1', v_2') \right\| = 0. \tag{128}$$

In this secular equation, all elements of H_1' which are non-diagonal with respect to l vanish on account of (49), since H_1' is independent of the angle φ. From the properties of the wave functions $\psi_{v_1}(\sigma)$ and $\psi_{v_2 l}(\varrho, \varphi$ as given in §1, and from the values of the integrals given in (20) and (50), it can easily be shown that the only non-vanishing elements of H_1' are the following

$$H_1' \, (v_1 \, v_2 l; v_1 \, v_2 l) = h\Delta \, (v_1 + \tfrac{1}{2}),$$

$$H_1' \, (v_1 \, v_2 l; v_1 - 1, v_2 + 2, l) = -\frac{hb}{\sqrt{8}} \sqrt{v_1} \sqrt{(v_2 + 2)} - l^2. \tag{129}$$

From (128) and with these values, one can calculate the energy changes for any values of $2v_1+v_2$. As an example, let us take $2v_1+v_2=4$. The secular equation is as follows:

$$\begin{array}{ccc|ccc|ccc|ccc}
 & & l & 0 & 0 & 0 & 2 & 2 & 4 & -2 & -2 & -4 \\
 & & v_2 & 0 & 2 & 4 & 2 & 4 & 4 & 2 & 4 & 4 \\
l & v_2 & v_1 v_1 & 2 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
\hline
0 & 0 & 2 & \cdots & \cdots & 0 & & & & & & \\
0 & 2 & 1 & \cdots & \cdots & \cdots & & & & & & \\
0 & 4 & 1 & 0 & \cdots & \cdots & & & & & & \\
\hline
2 & 2 & 1 & & & & \cdots & \cdots & & & & \\
2 & 4 & 0 & & & & \cdots & \cdots & & & & \\
4 & 4 & 0 & & & & & & \cdots & & & \\
\hline
-2 & 2 & 1 & & & & & & & \cdots & \cdots & \\
-2 & 4 & 0 & & & & & & & \cdots & \cdots & \\
-4 & 4 & 0 & & & & & & & & & \cdots
\end{array} \tag{130}$$

All the elements outside the sub-determinants vanish. The two quadratic factors of the equation give two roots repeated since the energy E' cannot depend on the sign of l. Similarly the two linear factors give two identical roots. The cubic factor gives three roots. Thus there are six distinct levels, grouped as follows:

$$\begin{array}{ccc} l = 0 & l = \pm 2 & l = \pm 4 \\ \left\{\begin{array}{r} 2\nu_1 \\ \nu_1 + 2\nu_2 \\ 4\nu_2 \end{array}\right. & \left\{\begin{array}{r} \nu_1 + 2\nu_2 \\ 4\nu_2 \end{array}\right. & 4\nu_2 \end{array} \tag{131}$$

The following table gives the first order energies for values of $2v_1 + v_2 = 0, 1, 2, 3. 4$.

v_1	v_2	l	$x = E'/h$
0	0	0	$\Delta/2$
0	1	± 1	$\Delta/2$
1	0	0	$\Delta \pm \frac{1}{2}\sqrt{\Delta^2 + 2b^2}$
0	2	0	
0	2	2	$\Delta/2$
1	1	± 1	$\Delta \pm \frac{1}{2}\sqrt{\Delta^2 + 2b^2}$
0	3	± 1	
0	3	± 3	$\Delta/2$
2	0	0	$x^3 - \frac{9}{2}\Delta x^2 - (3b^2 - 2\frac{3}{4}\Delta^2)x - 1\frac{5}{8}\Delta^3 + 1\frac{1}{2}b^2\Delta = 0$
1	2	0	
0	4	0	
1	2	± 2	$\Delta \pm \frac{1}{2}\sqrt{\Delta^2 + 6b^2}$
0	4	± 2	
0	4	± 4	$\Delta/2$

Table II

The total energy is now, instead of (86),

$$E^\circ + E' + E'' = h\,[x' + \nu_1 v_1 + \cdots\cdots x_{23}\, v_2\, v_3] + E'. \tag{132}$$

After having found the energies, it is of interest to consider the wave functions of the resulting states whose energies are given in Table II. According to the quantum mechanics, the perturbation H_1' in

(127) which is a non-diagonal matrix with respect to the wave functions $\psi_{v_1}(\sigma)$ and $\psi_{v_2 l}(\varrho,\varphi)$ is transformed into a diagonal matrix with respect to some other wave functions which are linear combinations of the zeroth order wave functions of the degenerate states, and the diagonal elements of H_1' in the new representation are given by the secular equation (128). Corresponding to each root of the secular equation, one can obtain a proper combination of the original wave functions. Consider the degenerate states v_1, v_2, $l=1,0,0$ and $0,2,0$. It is seen from Table II that the roots of (128) are $\Delta + \frac{1}{2}\sqrt{\Delta^2 + 2b^2}$ and $\Delta - \frac{1}{2}\sqrt{\Delta^2 + 2b^2}$. Let the wave functions corresponding to them be denoted by ψ_+ and ψ_- respectively. Then one readily obtains, if $y = \frac{\Delta}{|b|} < 1$,[3]

$$\psi_+ = \alpha\,\psi_1(\sigma)\,\psi_{00}(\varrho,\varphi) - \beta\,\psi_0(\sigma)\,\psi_{20}(\varrho,\varphi),$$

$$\psi_- = \beta\,\psi_1(\sigma)\,\psi_{00}(\varrho,\varphi) + \alpha\,\psi_0(\sigma)\,\psi_{20}(\varrho,\varphi), \tag{133}$$

where

$$\alpha^2 = \tfrac{1}{2}\left(1 + \frac{1}{\sqrt{2}}\,y\right), \qquad \beta^2 = \tfrac{1}{2}\left(1 - \frac{1}{\sqrt{2}}\,y\right). \tag{134}$$

Similarly, for the states v_1, v_2, $l=1,1,\pm1$ and $0,3,\pm1$, the wave functions corresponding to the two levels in Table II are

$$\Delta + \tfrac{1}{2}\sqrt{\Delta^2+2b^2} \;:\quad \psi_+ = \alpha\,\psi_1(\sigma)\cdot\psi_{11}(\varrho,\varphi) - \beta\,\psi_0(\sigma)\psi_{31}(\varrho,\varphi),$$

$$\Delta - \tfrac{1}{2}\sqrt{\Delta^2+2b^2} \;:\quad \psi_- = \beta\,\psi_1(\sigma)\,\psi_{11}(\varrho,\varphi) + \alpha\,\psi_0(\sigma)\psi_{31}(\varrho,\varphi). \tag{135}$$

where α and β are the same as in (134). Similar calculations can be carried out for other degenerate states. It is seen that each of the resulting states in a group of degenerate states is described by a mixture of the wave functions of the original states, in a proportion depending on the ratio of the resonance discrepancy Δ and the interaction term b, and also on the quantum numbers of the degenerate states in ques-

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[3] The coefficients α and β are obtained from the normalization condition $\int \overset{*}{\psi}_+ \cdot \psi_+ \, d\tau = \alpha^2 + \beta^2 = 1$ together with the condition that

$$\int \overset{*}{\psi}_+ H_1' \,\psi_+ \, d\tau = \alpha^2 \int \overset{*}{\psi}_1(\sigma) \cdot H_1'\, \psi_1(\sigma)\, d\sigma + 2\alpha\beta \int \overset{*}{\psi}_1(\sigma) \cdot \overset{*}{\psi}_{00}(\varrho\varphi) H_1' \psi_0(\sigma) \cdot \psi_{20}(\varrho,\varphi)\, d\tau$$

$$+ \beta^2 \int \overset{*}{\psi}_0(\sigma)\; H_1'\, \psi_0(\sigma)\, d\sigma = \Delta + \tfrac{1}{2}\sqrt{\Delta^2 + 2b^2}$$

tion. This mixing of the wave functions of the interacting degenerate states means a mutual sharing of the properties of these states. Thus because of the presence of the wave function $\psi_1(\sigma)$ in both of the states ψ_+ and ψ_-, the transitions from the normal state 0,0,0 to the pair of states 1,0,0 and 0,2,0 would give two Raman lines whose intensities are in the ratio of the squares of the matrix elements of the induced electric moment, *i.e.*, $\alpha^2 : \beta^2$ or $(1+ \frac{1}{\sqrt{2}} y)/(1- \frac{1}{\sqrt{2}} y)$. When y is small, as we shall later see this is the case with CO_2, the two Raman lines may have comparable intensities. Detailed application of the theory of this section to the CO_2 molecule will be taken up in Chap. V. There we shall see that similar situation obtains also in the case of the parallel vibration ν_1 and the first harmonic of the perpendicular vibration ν_4 of the methyl halides.

Finally we wish to emphasize that the mere equality or close proximity of two energy levels does not necessarily give rise to such resonance effects; only when the two levels in question have the proper symmetry properties would resonance interaction arise. This is already clear from (127) and (128); for if the symmetry properties of the two states are such that all the non-diagogal elements of the interacting potential (namely the term in b) vanish, then no resonance effects arise since no further diagonalization of H_1' is needed. To illustrate this, let us take the two normal vibrations ν_2 and ν_3 of the acetylene C_2H_2 molecule (see Chap. V, section on C_2H_2 for the modes of vibrations). The frequencies ν_2 and ν_3 are primarily determined by the valence force between the carbon and the hydrogen atoms, their difference being due to the interaction of the two C-H groups. Hence in the initial approximation we may put $\omega_2 = \omega_3$, and in the first approximation, $\omega_2 = \omega_3 + \Delta$. Since we are now only concerned with the vibrations ν_2 and ν_3, let us write down that part of the Hamiltonian that depends on the coordinates y_2 and y_3 of these two vibrations, namely,

$$\overset{\circ}{H}_1 = -\frac{h}{8\pi^2\omega_3}\left[\dot{y}_2^2 + \dot{y}_3^2\right] + \tfrac{1}{2} h\omega_3\left[y_2^2 + y_3^2\right]. \tag{136}$$

The first order Hamiltonian is similar to (127), namely,

$$H_1' = -\frac{h\Delta}{2}\ \frac{\partial^2}{\partial y_2^2} + \frac{h\Delta}{2}\ y_2^2 + hiy_2y_3^2. \tag{137}$$

The interaction consists of only the term $iy_2y_3^2$ since the potential must be an even function of y_3 (see Chap. V). That part of the zeroth order energy depending on v_2 and v_3 is easily seen to be

$$E_1^\circ = (v_2 + v_3 + 1)\,h\omega_3. \tag{138}$$

The degenerate states are those corresponding to the same value of v_2+v_3. The first order energy changes are given by the secular equation

$$\left\| H_1'\ (v_2, v_3; v_2', v_3') - E_1'\,\delta\,(v_2, v_3; v_2', v_3') \right\| = 0 \tag{139}$$

in which $v_2+v_3=v_2'+v_3'$. Since ψ_{v_2} is a solution of (60), it follows that

$$H_1'\,\psi_{v_2}(y_2) = h\left[iy_2\,y_3^2 + (v_2 + \tfrac{1}{2})\,\Delta\right]\cdot\psi_{v_2}(y_2)$$

and hence all the matrix elements of H_1' not diagonal with respect to both v_2 and v_3 vanish, and the non-vanishing diagonal elements are simply $(v_2+\frac{1}{2})h\Delta$. This shows that no resonance interaction arises between ν_2 and ν_3.

For the same reason, in spite of the numerous instances in which two energy levels are very close to each other or even coincident, only in a relatively few cases do resonance interactions arise.

§5. Vibrational Spectra and Molecular Structure

From the study of the vibrational spectra of molecules, one can establish their geometry and dimensions through considerations of the symmetry properties and selection rules and the rotational structures of the bands. Besides these, it is possible to derive some informations concerning the electronic structure of the molecule, or the state of polymerization, and to calculate the thermodynamical functions such as the entropy and free energy from the vibrational spectra. It is beyond the scope of this volume to enter into the extensive work that has been done on these subjects. We shall only indicate briefly in this section the kinds of informations and the way in which they can be obtained from the vibrational spectra.

A) Quantum-mechanical Resonance among Canonical Structures

The problem of determining the electronic structure of a polyatomic molecule is a difficult one. On the theoretical side, certain qualitative results can be obtained with relative ease; but quantitative calculations, in particular, of the "bond constants" by means of the wave mechanics, are so laborious that they have not been carried out for any except the simplest of the diatomic molecules. On the experimental side, a determination of the potential functions from the electronic bands, such as is done for the diatomic molecules, is beset by the difficulties (*i*) of observing discrete band spectra in the majority of the polyatomic molecules (comparatively few polyatomic molecules have discrete band spectra), and (*ii*) of analyzing the spectra when they are observed, on account of their complexities. One may expect, on quite general grounds, however, that a given electronic state is characterized by a potential function which determines the intramolecular distances, the frequencies of the vibrations, and the energies of dissociation of the molecule into various atoms and radicals. From the vibrational frequencies, it is possible to determine a zeroth-order approximation (quadratic) to this potential about the position of equilibrium, and from the rotational structure of the vibration-rotational bands it is often possible to obtain the intra-molecular distances, (see Chap. IV, §§1, 2). For example, the constants of the quadratic potentials for the C$-$C, C$=$C, C$\equiv$C bonds in a large number of molecules have the approximate values 5, 10, 15×10^5 dynes/cm and the bond distances 1.54, 1.33, 1.19 A respectively. Although purely theoretical relations connecting these bond lengths, bond constants and electronic structures are lacking, as mentioned before, quite definite semi-empirical relations between the bond structure (*i.e.*, single, double or triple bonds) and the bond lengths have been found by Pauling and his coworkers[1]. Also empirical relations between the bond constants and the bond lengths have been proposed, of which the most useful one is perhaps that of Badger[2]. A departure of the constants in a molecule from the "normal" values will hence indicate a different electronic structure in the molecule.

Besides the conspicuous differences in the values of the bond constants and bond lengths for single, double and triple bonds, it has been found that in a number of molecules both the vibrational spectra and the electron diffraction measurements yield values for the bond constants and bond lengths which differ appreciably from their "normal" values according to the classical concept of chemical valence. Thermochemical measurements also indicate in such cases a greater stability *i.e*., a greater value for the energy of dissociation) over the "normal" bonds. The explanation of such departures is furnished by the quantum-mechanical concept of resonance[3]. A detailed and quantitative treatment cannot be given here; but the idea can be readily described in a qualitative manner as follows: In the quantum mechanics, each state of a system is described by an eigen function. When there exist more than one states whose energies are equal (degenerate states) or nearly equal (partially degenerate), and if there exist interactions between them, the eigen functions of the states are then given by linear combinations of the eigen functions of the original states, the proportions of the different eigen functions in the combinations being determined by the energy differences between the states involved and the interactions between them. As the result of this "resonance", each state will contain the properties of the other states, and the lowest state will in general possess an energy which is lower than any one of the original states. (This is quite analogous to the case of resonance interactions between vibrational states discussed in §4). Consider for example the CO_2 molecule. The bond distance and bond constant for C-O in the molecule have values intermediate between those expected of double $C{=}C$ bond and triple $C{\equiv}C$ bond (see Chap. V, on CO_2). The explanation is that the eigen function of the normal state of the molecule consists of a linear combination of the eigen functions of the following structures

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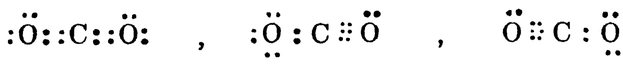
[1] L. Pauling, L. O. Brockway & J. Y. Beach, Jour. Am. Chem. Soc. 56, 2706, (1935).

[2] R. M. Badger, Jour. Chem. Phys. 3, 710, (1935); D. Clark, Phil. Mag. 18, 459, (1934); Clark and Stoves, ibid., 22, 1137, (1936); G.B.B.M. Sutherland, Proc. Ind. Acad. Sci., Raman Jubilee Volume, (1938).

$$O{=}C{=}O \quad , \quad O{-}C{\equiv}O \quad , \quad O{\equiv}C{-}O$$

or



$$:\overset{\cdot\cdot}{O}::C::\overset{\cdot\cdot}{O}: \quad , \quad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:C\,\vdots\vdots\,\overset{\cdot\cdot}{O} \quad , \quad \overset{\cdot\cdot}{O}\,\vdots\vdots\,C:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

and that the shortening of the $C{=}O$ bond due to the contribution of the triple bond character is greater than the lengthening of the bond due to the single-bond contribution. Another well known example is the $C{-}C$ bond in the benzene molecule (see Chap. V). From the relations of Pauling[1], it is possible to estimate the percentages of the different bond contributions from the measured bond distances.

We should perhaps emphasize, however, that while the bond distances can often be determined within narrow limits from electron diffraction measurements for the heavy molecules and from the structures of the vibration-rotational bands for the simpler and light molecules, informations concerning the electronic structure derived from the bond constants are subject to the following uncertainties: (*i*) In polyatomic molecules, the values of the potential constants ordinarily calculated do not have strictly unique meanings since their values depend on the forms of the potential chosen and since there is always an ambiguity inherent in the choice of the potential, and (*ii*) In relatively few molecules are available sufficient data that permit a correction of the observed frequencies for anharmonicity to be made and the couplings between the various atoms (represented by cross terms in the potential) to be included. It is for these reasons that great care must be exercised in basing conclusions concerning the bond structures on the bond constants alone.

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[3] Cf. L. Pauling, Jour. Am. Chem. Soc. 54, 3570, (1932); Proc. Nat. Acad. Sci. 18, 293, (1932); Pauling & G. W. Wheland, Jour. Chem. Phys. 1, 362, (1933); Pauling & J. Sherman, *ibid.*, 1, 606, 679, (1933); Wheland, *ibid.*, 1, 731, (1933); **3**, 230, (1935); Sherman, *ibid.*, 2, 488, (1934); G. W. Penney, Proc. Roy. Soc. A **146**, **223**, (1934).

B) Molecular Association

From the spectra of a large number of molecules, it has been abundantly demonstrated that a chemical bond or radical possesses frequencies characteristic of the bond or radical. This is due to the circumstance that in molecules, the bindings between the atoms in a chemical bond or radical are in general very much stronger than those between atoms not directly joined by chemical valence bonds. Thus a $\equiv C-H$ bond in a molecule is always accompanied by a frequency at ca. 3200 cm^{-1}, a $C-H$ bond with an unsaturated carbon atom by a frequency at ca. 2950 cm^{-1}, and $O-H$ bond by a frequency at 3600 cm^{-1}, etc.[1] It is found, however, that in the spectra of some molecules in the liquid state, these "characteristic frequencies" are shifted by 200-500 cm^{-1}, to the low frequency side (see Chap. V, sections on $HCOOH$ and CH_3OH). It is also found that these shifted bands decrease in intensity with the rise of temperature and upon dilution with other solvents, while the unshifted bands increase in intensity. The explanation is that in the liquid state, the molecular associations arising from the formation of the socalled hydrogen bonds (or other types of association) change the electronic structures of the bonds and hence their characteristic frequencies. For example, in the case of formic acid $HCOOH$, the study of the spectra at different temperatures establishes the dimer $(HCOOH)_2$, which derives its stability possibly from the quantum-mechanical resonance between the structures

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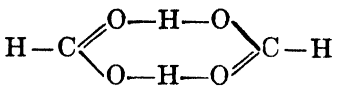
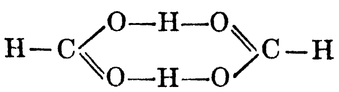
[1] See Kohlrausch, *Der Smekal-Raman* Effekt, and the Ergänzungsband, for such characteristic frequencies; also Chap. V below.





As a result of this association, the O-H band at 3570 cm^{-1} observed in the vapor is shifted to a band at 3080 cm^{-1} in the liquid. Other types of associations have been studied by a number of authors. We shall refer the reader to the literature[2]. Suffice it to say here that the study of the vibrational spectra provides a means of investigating the state of molecular associations in the liquids.

C) Thermodynamic Functions from Spectroscopic Data

Another field in which the study of the vibrational spectra of molecules has proved useful is the determination of the thermodynamic functions, such as the entropy and the free energy, of the molecules. When these functions are known over a certain range of temperature, it is possible to derive from them such quantities as the equilibrium constants of chemical reactions and the molecular heats. On the other hand, from the thermally measured values of the entropies or specific heats, it is possible to determine certain unknown frequencies, or at least to estimate them within certain limits, in a molecule. In the following, we shall summarize the general procedure of such calculations, but refer to the literature for the theory and the details of the methods employed in the actual calculations[1].

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[2] R. Freymann, C. R. 195, 39, (1932); Ann. de Physique 20, 243, (1933), alcohols and acids; J. Errera & P. Mollet, Jour. de Phys. et Rad. 6, 2811, (1935), fatty acids; C. R. 204, 259, (1937), ethyl alcohol; Errera, Trans. Faraday Soc. 33, 122, (1937), CCl_4 on alcohol; R. M. Badger & S. H. Bauer, Jour. Chem. Phys. 5, 839, (1937); Bauer & Badger, *ibid.*, 5, 852, (1937), the second harmonic of O-H band in a number of molecules; R. Barnes, L. G. Bonner & E. U. Condon, *ibid.*, 4, 772, (1936); A. M. Buswell, V. Deitz & W. H. Rodebush, *ibid.*, 5, 501, (1937); R. Gillette & A. Sherman, Jour. Am. Chem. Soc. 58, 1135, (1936); M. & R. Freymann, Bull. Soc. Chim. Franc. 4, 944, (1937); on hydrogen bond. Other references are given by R. Freymann, Jour. Chem. Phys. 6, 497, (1938).

[1] For the general theory, see Fowler's *Statistical Mechanics*, chapters II and III, (1936); for a review of the calculations of thermodynamic functions from spectroscopic data, see L. S. Kassel, Chem. Rev. 18, 277, (1936); also W. F. Giauque, Jour. Am. Chem. Soc. 52, 4808, (1930); J. E. Mayer, S. Brunauer & M. G. Mayer, *ibid.*, 55, 37, (1933), gave a discussion of the symmetry number; L. S. Kassel, *ibid.*, 55, 1351, (1933), gave some approximate expressions for the partition functions; Kassel, Jour. Chem. Phys. 1, 576, (1933), gave some asymptotic expansions for the partition functions; A. R. Gordon, *ibid.*, 1, 297, (1933), gave tables for the calculation of thermodynamic functions; G. M. Murphy, *ibid.*, 5, 673, (1937), gave some analytic expressions for the entropy and the free energy of a number of molecules.

Consider a molecule whose energy states are ε_0, ε_1, ε_2......with the statistical weights g_0, g_1, g_2, ... The energy of one gram-molecule of the substance is

$$E - E_0 = \frac{\Sigma\, \varepsilon_i g_i e^{-\frac{\varepsilon_i}{kt}}}{\Sigma\, g_i e^{-\frac{\varepsilon_i}{kt}}}, \tag{140}$$

(Here and in what follows, quantities with the subscript 0 are the values of the quantities at 0° K). On defining the partition function (or the Zustandssumme, or the state sum) Q by

$$Q = \Sigma\, g_i\, e^{-\frac{\varepsilon_i}{kT}}, \tag{141}$$

then

$$E - E_0 = - R\frac{d\, lnQ}{d\left(\frac{1}{T}\right)}. \tag{142}$$

The contribution to the specific heat of the molecule by these energy levels is[2]

$$C_v = \frac{dE}{dT} = R\left(\frac{1}{T}\right)^2 \frac{d^2 lnQ}{d\left(\frac{1}{T}\right)^2}, \tag{143}$$

and the contribution to the entropy is

$$S - S_0 = \int_0^T dS = R\left[\, ln\, Q - \frac{1}{T}\, \frac{dln\, Q}{d\left(\frac{1}{T}\right)} - lng_0\right], \tag{144}$$

where $S_0 = R\, ln\, g_0$ may be called the zero-point entropy.

Because of the fact that the energy of molecule can be written as the sum of translational, rotational and vibrational energies, and as

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[2] In the case of translational motions, (143) gives simply the classical result $C_v = \frac{1}{2}3R$, since the energies although quantized are practically continuous for molecules moving in a vessel of ordinary dimensions. For simple harmonic vibration of frequency ν, (143) gives simply the well known Einstein formula

$$C_v = R\,\frac{x^2\, e^x}{(e^x - 1)^2}, \quad x = \frac{h\nu}{kT}.$$

the different energies contribute multiplicatively to the partition function Q and hence additively to the entropy, we may write[3]

$$S = S_{trans} + S_{vib} + S_{rot} + S_{spin} + S_{\sigma} , \qquad (145)$$

where S_{spin} is the entropy due to the spin weight of the molecule, and S_{σ} is the entropy due to the possibility of rotating the molecule and still leaving it look alike.

The translational entropy of one gram-molecule of a gas of molecular weight M at a temperature T and a pressure P (in atmospheres) is given by the Sackur-Tetrode equation[4]

$$S_{trans} = R \ln \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \cdot e^{\frac{5}{2}}$$

$$= \tfrac{3}{2} R \ln M + \tfrac{5}{2} R \ln T - R \ln P + C, \qquad (146)$$

where

$$C = \tfrac{5}{2} R + R \ln R' + R \ln \frac{(2\pi k)^{\frac{3}{2}}}{h^3 N^{5/2}} = - 2.30 \text{ cal/mole/degree}$$

and R' is the gas constant in cc. atm./degree.

The vibrational entropy for a harmonic oscillator of frequency ν is

$$S_{vib} = R\left[\frac{x}{e^{x}-1} - \ln(1 - e^{-x})\right], \qquad (147)$$

where

$$x = \frac{h\nu}{kT} .$$

The total vibrational entropy of the molecule is obtained by summing (147) over all the normal vibrations of the molecule.

The rotational entropy must be calculated from (141) and (144) in which the energies are the rotational energies of a linear rotator, a symmetrical rotator or an asymmetrical rotator depending on the nature of the molecule under consideration. These energies are given by (4), (25) and (35), respectively, of Chap. IV. In general, the evaluation of the partition function for these energies is a tedious, if not difficult, process. In the limit of large values of the moments of inertia, one may replace the summation in (141) by integration and obtain quite simply, for a linear molecule,[5]

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[3] We shall confine ourselves to the normal electronic state of the molecule in these calculations since the contributions of the excited electronic states to the thermodynamic quantities are negligible. Also the nuclear spins of the atoms in the molecule are considered only in so far as they modify the statistical weights of the enery states.

[4] Cf. R. H. Fowler, *Statistical Mechanics*, P. 56 ff. (1936).

$$S_{rot} = R\,ln\left(\frac{8\pi^2 I\,kT}{h^2}\right)\cdot e, \tag{148}$$

and for a molecule possessing three different principal moments of inertia A, B, C,[5]

$$S_{rot} = R\,ln\left[\frac{8\pi^2(ABC)^{\frac{1}{2}}(\pi\,kT)^{\frac{3}{2}}}{h^3}\right]e^{\frac{3}{2}}. \tag{149}$$

The nuclear spin entropy S_{spin} is given by

$$S_{spin} = R\,ln\,p_n, \tag{150}$$

where p_n is the spin weight, and is equal to $\Pi_i\,(2s_i+1)$ where s_i is the spin of the nucleus *i*. In CH_4, for example, $p_n=2^4=16$; in C_2H_6, $p_n=2^6=64$. This part of the entropy is independent of temperature and enters only as an additive constant in the total entropy. For $S\sigma$, one has

$$S\sigma = -R\,ln\,\sigma, \tag{151}$$

where σ is the so-called symmetry number. It is the number of permutations of identical particles in the molecule that can be carried out by changes in the coordinates of rotation and nuclear spin alone.

In the next approximation, the vibrational and the rotational entropies given by (147) and the quantum-theory expressions for (148) and (149) must be corrected for (*i*) the anharmonicity of the vibrations, and (*ii*) the interactions between the vibrational and the rotational motion of the molecule. The energy of vibration of a polyatomic molecule must then be expressed by an expression of the form (86), and the interaction between the vibration and the rotation is taken into account by an expression of the form (96) of Chap. IV. These corrections further complicate the evaluation of the partition function in (141); but in general, their effect is small and can be neglected in a first approximation.

The free energy F is defined by

$$F = H - TS \tag{152}$$

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[5] Fowler, *loc. cit.*, Pp. 62, 63 (1936).

where H is the energy content. For the vibrational motion, for example, one obtains from (142), (144) and (147)

$$\frac{F}{T} = -R \ln Q = R \ln(1 - e^{-x}). \tag{153}$$

For motions including translational, vibrational and rotational motions,

$$H = E_{trans} + E_{vib} + E_{rot} + PV = E + \tfrac{5}{2} RT \tag{154}$$

where E is given by (142) in which the partition function includes those for the vibrational and the rotational motions, and $PV=RT$ for an ideal gas. From (146), one obtains[6]

$$\begin{aligned} -\frac{(F-E_o)}{T} &= R\left[\tfrac{3}{2} \ln M + \tfrac{5}{2} \ln T - \ln P + \ln Q\right] + C - \tfrac{5}{2} R \\ &= R\left[\tfrac{3}{2} \ln M + \tfrac{5}{2} \ln T - \ln P + \ln Q\right] - 7.267. \end{aligned} \tag{155}$$

Recently, calculations of the entropy and the free energy from spectroscopic data have been carried out for a number of molecules[7]. Of particular interest are the calculations of the entropies of the ethane and the benzene molecules. These will be further mentioned in the corresponding sections on these molecules in Chap. V.

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[6] The spin and the symmetry entropies in (150) and (151) have not been included in (155) for simplicity.

[7] L. S. Kassel, Jour. Am. Chem. Soc. 56, 1838, (1934), CO_2, N_2O; Jour. Chem. Phys. 3, 115, (1935); $C(CH_3)_4$; A. R. Gordon & C. Barnes, *ibid.*, 1, 297, 308, 692, (1933), H_2O, CO_2, HBr, Br_2; Gordon, *ibid.*, 2, 65, 549, (1934), steam; *ibid.*, 3, 259, 336, (1935), HCN, N_2O, C_2H_2, SO_2; R. C. Lord & E. E. Blanchard, *ibid.*, 4, 707, (1936), CCl; Lord, J. E. Ahlberg & D. H. Andrews, *ibid.*, 5, 649, (1937), specific heat of benzene; D. P. Stevenson & J. Y. Beach, *ibid.*, 6, 25, 108, 341, (1938), H_2CO, $COCl_2$, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4; Gordon, *ibid.*, 6, 219, (1938), C_2H_2; B. L. Crawford & P. C. Cross, *ibid.*, 6, 525, (1938) $Ni(CO)_4$; J. W. Linnett & W. H. Avery, *ibid.*, 6, 686, (1938), allene; Linnett, *ibid.*, 6, 692, (1938), cyclopropane; Crawford & J. T. Edsall, *ibid.*, 7, 223, (1939), $B_3N_3H_6$; Lord & Andrews, Jour. Phys. Chem. 41, 149, (1937), benzene; for calculations of the entropy and specific heat of ethane, see footnote (5) in section on C_2H_6, Chap. V.

CHAPTER IV

VIBRATION-ROTATIONAL SPECTRA OF MOLECULES

In our discussion of the quantum theory of the vibrations of molecules, we have so far neglected the simultaneous change in the rotational state of the molecules. As shown in §4, Chap. II, the simultaneous change of the vibrational and the rotational states give rise to a vibration-rotational band, the structure of which is determined by (1) the moments of inertia of the molecule, (2) the symmetry properties of the molecule, and (3) the direction of the change of the electric moment relative to the elements of symmetry of the molecule. The classical theory predicts, however, a continuous distribution of the rotational frequencies in disagreement with the observed discrete structure. Hence a treatment of the vibration-rotational bands according to the quantum theory is necessary. In this chapter, we shall indicate the theoretical methods for treating such problems as the energies and the intensities of the transitions involving simultaneous changes in both the vibrational and the rotational states in different types of molecules, and summarize the results upon which our discussions of the individual molecules in Chap. V are based. For further details, we must refer the reader to the treatments by Dennison[1] and by Teller.[2]

§1. **Pure Rotational Spectra**

Let us first consider only the rotational motions of polyatomic molecules in the order of the simplicity in their mathematical treatments, namely, (A) linear molecules, (B) symmetrical rotators, and (C) asymmetrical rotators.

A). Linear molecules

The quantum theory of a rigid linear rotator is well known. Consider a rotator whose moment of inertia about the center of gravity is I. The Schroedinger equation for the free rotation of the molecule about the c. g. is

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{8\pi^2 I}{h^2}E\psi=0, \tag{1}$$

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[1] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

[2] E. Teller, *Hand-und Jahrbuch der chemischen Physik* 9/II, (1934).

where ϑ and φ are the polar angles. On assuming $\Psi(\vartheta,\varphi) = \Phi(\varphi)\,\Theta(\vartheta)$ and requiring the wave function to be single-valued in φ, one obtains

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi, \qquad \Phi = \frac{1}{\sqrt{2\pi}}\, e^{im\varphi}, \tag{2}$$

$$\frac{d}{dx}\left[(1-x^2)\frac{d\Theta}{dx}\right] + \left[\frac{8\pi^2 IE}{h^2} - \frac{m^2}{1-x^2}\right]\Theta = 0, \quad x = \cos\vartheta, \tag{3}$$

where m is an integer, either positive or negative. On requiring the function $\Theta(\vartheta)$ to be finite for $\vartheta = 0$ and π, one obtains for the eigenvalues of equation (3) the following condition

$$E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1), \qquad J = 0, 1, 2. \tag{4}$$

The eigenfunctions are the orthogonal associated Legendre's polynomials which when normalized are

$$\Theta(\vartheta) = \sqrt{\frac{2J+1}{2} \cdot \frac{(J-|m|)!}{(J+|m|)!}}\; P_J^m(\cos\vartheta), \tag{5}$$

in which $|m| \leq J$. For each value of J, m can take on $2J+1$ values, namely, $-J, -J+1, \ldots 0, \ldots J-1, J$, and hence there are $2J+1$ independent wave functions on combining (2) and (5). Since the energy E_{rot} in (4) is independent of the value of the quantum number m, it follows that the state J is $(2J+1)$-fold degenerate, and has a weight of $2J+1$. It can be shown that the J and m have the following physical meanings: $J(J+1)(h/2\pi)^2$ is the square of the total angular momentum of the rotator and $m(h/2\pi)$ is the component of the angular momentum about the polar axis which is fixed in space. In the system in which the energy E_{rot} is a diagonal matrix (whose diagonal elements are given by equation (4) above), the square of the total angular momentum and the component of the angular momentum along the z-axis are also given by diagonal matrices.

To obtain the selection and the intensity rules, we have to consider the electric moment associated with various changes of the rotational state. Assuming that the rotator possesses a permanent electric moment $\mathfrak{M}_0$ along its axis, we can express the components of $\mathfrak{M}_0$ along the x, y, z axes which are fixed in space as follows:

$$\begin{aligned} \mathfrak{M}_z &= \mathfrak{M}_0 \cos\vartheta, \\ \mathfrak{M}_x + i\,\mathfrak{M}_y &= \mathfrak{M}_0 \sin\vartheta\, e^{i\varphi}, \\ \mathfrak{M}_x - i\,\mathfrak{M}_y &= \mathfrak{M}_0 \sin\vartheta\, e^{-i\varphi}. \end{aligned} \tag{6}$$

The matrix elements of these components associated with the transition between the two states J, m and J', m' have the following values, on account of the properties of the functions Φ and Θ in (2) and (5),

$$\mathfrak{M}_z(J,m;J',m')=\begin{cases}0 \text{ if } m\neq m',\ J'\neq J\pm 1,\\ \sqrt{\dfrac{(J+m)(J-m)}{(2J+1)(2J-1)}}\cdot\mathfrak{M}_0 \text{ if } m'=m,\ J'=J-1;\end{cases} \tag{7a}$$

$$(\mathfrak{M}_x+i\mathfrak{M}_y)(J,m;J',m')=\begin{cases}0 \text{ if } m'\neq m-1,\ J'\neq J\pm 1,\\ \sqrt{\dfrac{(J+m-1)(J+m)}{(2J+1)(2J-1)}}\cdot\mathfrak{M}_0 \text{ if } m'=m-1,\ J'=J-1;\end{cases} \tag{7b}$$

$$(\mathfrak{M}_x-i\mathfrak{M}_y)(J,m;J',m')=\begin{cases}0 \text{ if } m'\neq m+1,\ J'\neq J\pm 1,\\ \sqrt{\dfrac{(J-m-1)(J-m)}{(2J+1)(2J-1)}}\cdot\mathfrak{M}_0 \text{ if } m'=m+1,\ J'=J-1.\end{cases} \tag{7c}$$

In all the expressions under the radical signs, m means the absolute value of m. Similarly, the values of the matrix elements (7a), (7b) and (7c) for $J'=J+1$ are given below[3]

$$\mathfrak{M}_z(J,m;J+1,m)=\sqrt{\frac{(J+m+1)(J-m+1)}{(2J+1)\ (2J+3)}}\,\mathfrak{M}_0, \tag{8a}$$

$$(\mathfrak{M}_x+i\ \mathfrak{M}_y)(J,m;J+1,m-1)=\sqrt{\frac{(J-m+1)(J-m+2)}{(2J+1)\ (2J+3)}}\,\mathfrak{M}_0, \tag{8b}$$

$$(\mathfrak{M}_x-i\ \mathfrak{M}_y)(J,m;J+1,m+1)=\sqrt{\frac{(J+m+1)(J+m+2)}{(2J+1)\ (2J+3)}}\,\mathfrak{M}_0. \tag{8c}$$

From these it follows that the selection rules are

$$\Delta m=0,\pm 1, \qquad \Delta J=\pm 1 \tag{9}$$

and the absorption spectrum in the infrared consists of a number of equidistant lines whose frequencies are given by

$$\nu_r=\frac{h}{4\pi^2 I}(J+1)=2B\,(J+1),\quad J=0,1,2\cdots \tag{10}$$

---

[3] The matrix elements in (7) and (8) can be obtained with the aid of the following properties of the associated Legendre's polynomials

$$(2J+1)\cos\vartheta\ P_J^m=(J-m+1)P_{J+1}^m+(J+m)\ P_{J-1}^m$$

$$(2J+1)\sin\vartheta\ P_J^m=P_{J+1}^{m+1}-P_{J-1}^{m+1}$$

From the spacing $2B=(h/4\pi^2I)$ between two successive lines, it is possible to obtain the moment of inertia of the molecule.

To obtain the intensities of the rotational lines, it is necessary to know the following factors: (1) the relative population of the various rotational states as given by the Boltzmann theorem, (2) the weights of these states, and (3) the values of the matrix elements of the electric moment for the various transitions. Let $B(J\rightarrow J+1)$ be the Einstein coefficient of absorption (from state J to state $J+1$), and N_J the number of molecules per unit volume in the state J. Then the intensity of the absorption line $J\rightarrow J+1$ is given by

$$I(J\rightarrow J+1) = h\nu N_J\, B(J\rightarrow J+1)\,(1-e^{-\frac{h\nu}{kT}}), \tag{11}$$

where

$$N_J = N g_J\, e^{-\frac{E_J}{kT}} \Big/ (\sum_{J'} g_{J'}\, e^{-\frac{E_{J'}}{kT}}) \tag{12}$$

and

$$B(J\rightarrow J+1) = \frac{8\pi^3}{3h^2}\frac{g_{J+1}}{g_J}\left|\mathfrak{M}(J+1;J)\right|^2, \tag{13}$$

N is the number of molecules per unit volume, and g_J is the weight of the state J. The matrix element $\mathfrak{M}$ is given by

$$|\mathfrak{M}(J+1;J)|^2=|\mathfrak{M}_x(J+1;J)|^2+|\mathfrak{M}_y(J+1;J)|^2+|\mathfrak{M}_z(J+1;J|^2. \tag{14}$$

Since the energy E_n, and hence the frequency of the radiation of the transition $J\rightarrow J+1$, are independent of the quantum number m, it appears that in obtaining the intensity of the transition $J\rightarrow J+1$, it is necessary to consider all the possible transitions of m by summing over all values of m. This summing, however, is not necessary if one obtains the square of the matrix element $\mathfrak{M}(J+1;\ J)$ by adding the squares of the x, y, z components as in (14), the reason being that in forming the sum (14) all possible orientations of the rotator are automatically taken into account. This is also seen from the fact that by replacing J in (7a), (7b) and (7c) by $J+1$ to correspond to the transition $J+1\rightarrow J$ and substituting into (14), the result is

$$|\mathfrak{M}(J+1;J)|^2 = \frac{J+1}{(2J+3)}|\mathfrak{M}_0|^2, \tag{15}$$

which is independent of m. Hence (10) becomes

$$I(J \rightarrow J+1) = \frac{2\pi N (J+1)^2}{3I\,(\Sigma g_{J'} e^{-\frac{E_{J'}}{kT}})} \, |\mathfrak{M}_0|^2 \, e^{-\frac{hB}{kT}J(J+1)} \left(1 - e^{-\frac{h\nu}{kT}}\right). \quad (16)$$

It is seen from this expression that the intensities of the rotational lines of high values of J are small because of the Boltzmann factor, and those of the rotational lines of low values of J are also small because of the factor $(J+1)^2$. For a certain value of J depending on the moment of inertia I, the intensity is maximum.

B). Consider next a rigid symmetrical rotator which has an axis of symmetry, and whose principal moments of inertia are I_C and $I_A = I_B$. The problem of finding the energy and the selection and intensity rules has been worked out by a number of authors.[1] While the analysis is more complicated than what we have given for the linear rotator, the method is essentially the same. An admirable summary of the results has been given by Dennison.[2] We cannot do better here than follow his treatment.

Let a set of rectangular axes ξ, η, ζ be fixed in the rotator, with the ζ axis along the symmetry axis and the origin at the center of gravity of the rotator. The Schrödinger equation is best expressed in terms of the Euler's angles ϑ, φ, ψ defining the orientation of these axes with respect to the coordinate axes x, y, z which are fixed in space and have the same common origin as the ξ, η, ζ axes. The equation is[3]

$$\frac{\partial^2\Psi}{\partial\vartheta^2} + \cot\vartheta \frac{\partial\Psi}{\partial\vartheta} + \left(\frac{I_A}{I_C} + \cot^2\vartheta\right)\frac{\partial^2\Psi}{\partial\varphi^2} + \frac{1}{\sin^2\vartheta}\frac{\partial^2\Psi}{\partial\psi^2}$$

$$- 2\frac{\cos\vartheta}{\sin\vartheta}\frac{\partial^2\Psi}{\partial\psi\partial\varphi} + \frac{8\pi^2 I_A}{h^2} E\,\Psi = 0. \quad (17)$$

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[1] Matrix mechanical treatment by D. M. Dennison, Phys. Rev. 28, 318, (1926); wave mechanical treatments by F. Reiche and H. Radermaker, Zeits. f. Physik 39, 444, (1926); 41, 453, (1927); R. de I. Kronig and I. I. Rabi, Phys. Rev. 29, 262, (1927); C. Manneback, Phys. Zeits. 28, 72, (1927).

[2] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

[3] For a derivation of this equation, besides the original papers mentioned in footnote (1), see for example Sommerfeld's *Wave Mechanics*.

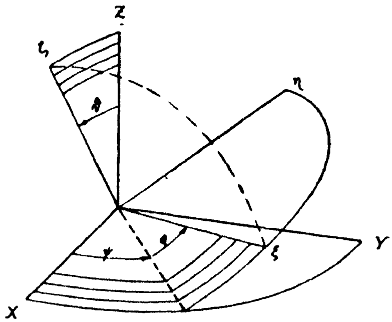

Fig. 16. Euler's angles

Since the angles φ and ψ are cyclic coordinates, we may assume

$$\Psi(\vartheta, \varphi, \psi) = \Theta(\vartheta) \cdot e^{iM\psi}\, e^{iK\varphi}, \tag{18}$$

where K and M must be integers, either positive or negative, in order that the wave function Ψ be single-valued. Substitution of (18) into (17) gives the equation for Θ

$$\Theta'' + \cot\vartheta\,\Theta' - \left(\frac{M-K\cos\vartheta}{\sin\vartheta}\right)^2 \Theta + \sigma\Theta = 0 \tag{19}$$

where

$$\sigma = \frac{8\pi^2 I_A}{h^2} E - \frac{I_A}{I_C} K^2. \tag{20}$$

This equation may be transformed, on introducing

$$\begin{gathered} s = |K+M|, \qquad d = |K-M|, \\ t = \sin^2\frac{\vartheta}{2}, \qquad \Theta = \sin^d\frac{\vartheta}{2}\cos^s\frac{\vartheta}{2}\,F(t), \end{gathered} \tag{21}$$

into the so-called hypergeometric equation

$$t(1-t)F'' + [\gamma - (\alpha+\beta+1)t]F' - \alpha\beta F = 0, \tag{22}$$

in which

$$\begin{gathered} \gamma = 1 + d. \qquad \alpha + \beta = 1 + d + s, \\ \alpha\beta = \frac{d+s}{2}\left(\frac{d+s}{2} + 1\right) - \sigma - K^2. \end{gathered} \tag{23}$$

The solution of (22) is the so-called hypergeometric function

$$F(\alpha, \beta, \gamma, t) = 1 + \frac{\alpha\cdot\beta}{1\cdot\gamma} t + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1\cdot 2\cdot\gamma(\gamma+1)} t^2 + \cdots\cdots. \tag{24}$$

The condition that the solution F be finite for all values of the variable requires this series to terminate at a certain power of t, say t^p. This requires that either α or β be equal to $-p$. Equations (20) and (23) then give the eigenvalues

$$E = \frac{h^2}{8\pi^2 I_A}\left[J(J+1) + \beta K^2\right] \tag{25}$$

in which

$$\beta = \frac{I_A}{I_C} - 1 \tag{26}$$

and

$$J = p + \tfrac{1}{2}(d + s). \tag{27}$$

From (21) and (27), it is seen that $|K| \leqq J$ and also $|M| \leqq J$. A detailed analysis shows that the quantum numbers J, K, M have the following physical meanings: $J(J+1)(h/2\pi)^2$ is the square of the total angular momentum, $K(h/2\pi)$ and $M(h/2\pi)$ are the components of the angular momentum about the symmetry axis and the space z-axis respectively. Hence for a given value of J, the quantum numbers K and M can each take on $2J+1$ values, namely, $-J, -J+1, \ldots J-1, J$. Since the energy E in (25) is independent of M and depends only on the square of K, it follows that the state J, K is $(2J+1)$-fold degenerate if $K=0$, and $2(2J+1)$-fold degenerate if $K \neq 0$.[4]

To obtain the selection rules of the rotator, we have to consider again the matrix elements of the components of the electric moment along fixed directions in space. We shall assume that the rotator possesses a permanent electric moment $\mathfrak{M}_0$ along the symmetry axis. The components of the electric moments along the x, y, z axes are again given by expressions similar to (6), in fact by

$$\mathfrak{M}_z = \mathfrak{M}_0 \cos\vartheta, \qquad \mathfrak{M}_x \pm i\mathfrak{M}_y = \mathfrak{M}_0 \sin\vartheta\, e^{\mp i\psi}.$$

From (18), we readily obtain the following selection rules

$$\mathfrak{M}_z(J,K,M;\, J',K',M') = 0 \quad \text{unless } K-K'=0, \quad M-M'=0,$$

$$(\mathfrak{M}_x \pm i\mathfrak{M}_y)(J,K,M;\, J',K',M') = 0 \quad \text{unless } K-K'=0, \quad M-M'=\pm 1.$$

The selection rules for J must be obtained by considering integrals of the form

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[4] As a special case of the symmetrical rotator, we may take the spherical rotator for which $I_A = I_B = I_C$. The energy of rotation is given by (25) with $\beta = 0$ and accordingly, the level J is $(2J+1)^2$—fold degenerate. As the permanent dipole moment is zero on account of the symmetry, such a spherically symmetrical rotator possesses no pure rotational spectrum.

$$\int \Theta_{JKM} \left\{ \begin{matrix} \cos\vartheta \\ \sin\vartheta \end{matrix} \right\} \Theta_{J'K'M} \cos\vartheta \, d\vartheta.$$

It can be shown that this integral vanishes unless $J-J'=0, \pm 1$. From these we obtain the selection rules for the pure rotational spectrum

$$\Delta J = 0, \pm 1, \qquad \Delta K = 0, \qquad \Delta M = 0, \pm 1. \tag{28}$$

The spectrum thus consists of a set of equidistant lines given by

$$\nu_r = \frac{h}{4\pi^2 I_A} (J+1), \quad J = 0, 1, 2, \cdots, \tag{29}$$

and is similar to that of a linear rotator of moment of inertia I.

To find the intensity of the absorption line $J \rightarrow J+1$, we have to calculate again the square of the matrix element of the electric moment for the transition $J+1 \rightarrow J$. As the energy of the rotator is independent of M, it again appears at first that one would have to take into account all possible transitions in M by summing the squares of the matrix elements over M from $-J$ to J. But this is not necessary if we form the sum of the squares of the x, y, z components of the electric moment as in (14), and in fact the result in this case is

$$|\mathfrak{M}(J+1, K; J, K)|^2 = \frac{(J+1)^2 - K^2}{(J+1)(2J+3)} |\mathfrak{M}_0|^2, \tag{30}$$

which is independent of M. Since the various transitions $K \rightarrow K$ give the same frequency, the intensity of the line $J \rightarrow J+1$ is given by (11), (12), (13) and (31)

$$I(J \rightarrow J+1) = \frac{2\pi N (J+1)^2 (1 - e^{-\frac{h\nu}{kT}})}{3 I_A (\sum_{J,K} g_{JK} e^{-\frac{E_{JK}}{kT}})} |\mathfrak{M}_0|^2 \sum_{K=-J}^{J} [1 - \frac{K^2}{(J+1)^2}] e^{-\alpha J(J+1) - \alpha\beta K^2}, \tag{31}$$

where $\alpha = h^2/(8\pi^2 I_A kT)$. It is seen that the intensities are small for both high values and low values of J, and that for a certain value depending on the moments of inertia I_A and I_C and also the temperature T, the intensity is maximum. It is also seen that (31) reduces, in the case of a linear rotator, *i.e.*, $I_C=0$ and $K=0$, to equation (16).

C) Let us finally consider a molecule in general, namely, one whose principal moments of inertia are all different, $I_A \neq I_B \neq I_C$. The problem of finding the energy of such a rotator and its selection and intensity rules has been investigated by a number of authors.[1] The mathematical treatment of the problem is more complicated than that of the symmetrical rotator. An excellent summary of the results has been given by Dennison.[2] We shall again refer to this article for details and shall confine ourselves here to a brief statement of the results.

Let the principal moments of inertia be $I_A < I_B < I_C$ and let the components of the angular momentum along these principal axes be P_A, P_B, P_C so that the Hamiltonian is

$$H = \tfrac{1}{2}\left[\frac{P_A^2}{I_A} + \frac{P_B^2}{I_B} + \frac{P_C^2}{I_C}\right]. \tag{32}$$

In a system in which the square of the total angular momentum $P^2 = P_A^2 + P_B^2 + P_C^2$ and also the component about the C axis P_C are given by diagonal matrices, *i.e.*,

$$\begin{aligned} P^2(J, K; J, K) &= J(J+1)\left(\frac{h}{2\pi}\right)^2 \\ P_C(J, K; J, K) &= K\left(\frac{h}{2\pi}\right), \end{aligned} \tag{33}$$

the Hamiltonian is non-diagonal. The non-vanishing elements are given by

$$\begin{aligned} &H(J,K;J,K) = \tfrac{1}{2}h(A+B)[J(J+1)-K^2] + CK^2, \\ &H(J,K;J,K+2) = \tfrac{1}{4}h(A-B)[(J-K)(J-K-1)(J+K+1)(J+K+2)]^{\frac{1}{2}}, \end{aligned} \tag{34}$$

where

$$A = (h/4\pi^2 I_A), \quad B = (h/4\pi^2 I_B), \quad C = (h/4\pi^2 I_C).$$

The energies of the rotator are then given by the diagonal elements of the Hamiltonian in a system in which it is a diagonal matrix, *i.e.*, by the secular equation

$$\left\| H(J, K; J, K') - E \;\delta(J, K; J, K') \right\| = 0,$$

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[1] E. Witner, Proc. Acad. Nat. 13, 60, (1927); S. C. Wang, Phys. Rev. 34, 243, (1929) gave a wave mechanical treatment of the asymmetrical rotator in which the energies are obtained from a secular equation. H. A. Kramers and G. P. Ittmann, Zeits. f. Phys. 53, 553; 58, 217, (1929); 60, 663, (1930) obtained the energies and the selection rules from the Lamé differential equations. O. Klein, Zeits. f. Physik 58, 730, (1929) gave the matrix mechanical treatment which is briefly outlined here after Dennison.

which on account of (34) looks as follows

$$\begin{array}{c|ccccccc:cccccc|l}
 & J & J-1 & & & & & -J & J' & J'-1 & & & & -J' & \\
J & * & 0 & * & 0 & 0 & & 0 & & & & & & & \\
J-1 & 0 & * & 0 & * & 0 & & 0 & & & & & & & \\
J-2 & * & 0 & * & 0 & * & 0 & 0 & & & & & & & \\
 & 0 & * & 0 & * & 0 & * & 0 & & & & & & & (35) \\
-J & 0 & 0 & 0 & 0 & 0 & & * & & & & & & & \\
\hdashline
J' & & & & & & & & * & 0 & * & 0 & & 0 & = 0. \\
J'-1 & & & & & & & & 0 & * & 0 & * & & 0 & \\
J'-2 & & & & & & & & * & 0 & * & 0 & & 0 & \\
 & & & & & & & & 0 & * & 0 & * & 0 & &
\end{array}$$

Since the determinant is diagonal in J, the equation separates into a number of sub-determinantal equations. For each value of J, the energies are given by the $(2J+1)$ roots of the sub-determinantal equation which can be expressed in terms of the parameters I_A, I_B, I_C. Explicit algebraic equations for the energies for values of J up to 11 have been tabulated by Kramers and Ittmann, Dennison, Nielsen,[3] and by Randall, Dennison, Ginsberg and Weber.[4] From these equations, one can calculate the rotational energy levels for any molecule with given values for the I_A, I_B, I_C. In Fig. 17 is indicated the connection between the $(2J+1)$ levels (for $J=3$) of an asymmetrical rotator and the $(J+1)$ distinct levels in the limiting cases of the symmetrical rotators $I_B=I_A$ and $I_B=I_C$. It is seen that the degeneracy in the levels $K\neq 0$ in the symmetrical rotators is removed in the case of the asymmetrical rotator. For convenience, the $2J+1$ levels are labelled with an indenx τ which takes the values from J to $-J$ in the order of decreasing energies.

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[2] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

[3] H. H. Nielsen, Phys. Rev. 38, 1432, (1931).

[4] Randall, Dennison, Ginsberg and Weber, Phys. Rev. 52, 162, (1937).

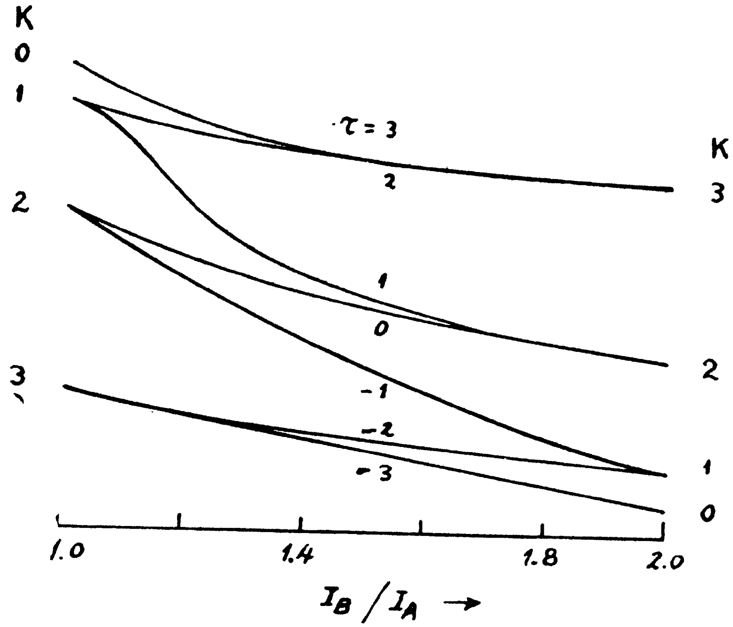

Fig. 17. Rotational energy levels (J=3) of an asymmetrical rotator

It is seen from the figure that when the rotator is only slightly asymmetric, *i.e.*, $I_B \simeq I_A$ (or $I_B \simeq I_C$), the $2J+1$ levels arrange themselves into narrow doublets, one for each value of $K \neq 0$ in the case of the symmetrical rotator $I_B = I_A$ (or $I_B = I_C$) in the limit. This suggests a perturbation calculation of the energy of a slightly asymmetrical rotator, in which the difference between the Hamiltonians of the two rotators is treated as a perturbation on the symmetrical rotator. This perturbation gives rise to a splitting of each level $K \neq 0$ of the symmetrical rotator into a doublet, the level $K=0$ remaining single. It is seen from Fig. 17 that the results of such a calculation are specially good for those levels with the largest values of K for which the splittings are small. We shall refer the reader to the original papers already cited and in particular to the works of Mecke[5] for further details.

The selection rules are again obtained from a consideration of the matrix elements of the components of the electric moment associated with various changes of the rotational state. For this purpose, one needs the wave functions of the asymmetrical rotator. The wave function for any state J, τ can be expressed as a linear combination of a proper set of the wave functions of the symmetrical rotator

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[5] R. Mecke, Zeits. f. Physik 81, 313, (1933); chapter in *Hand-und Jahrbuch der chemischen Physik* 9/II, (1934).

$$\psi_{J,\tau,M} = \Sigma\, C^{K}_{J,\tau,M,}\ \psi_{J,K,M} \qquad (36)$$

in which the coefficients are given by the minors of the determinant in (35). The symmetry properties of these wave functions, that is, the behavior of the wave functions upon certain operations on the rotational coordinates, can then be obtained by examining the properties of the wave functions of the symmetrical rotator. The results of a detailed investigation are the following:

Let a coordinate system be fixed in the rotator, with the ξ, η, ζ axes along the principal axes of moment of inertia I_A, I_B, I_C respectively. We shall consider two operations: (a) rotation about the ζ axis through π, and (b) a rotation about the ξ axis through π. With respect to the the operation (a), the wave function of the highest level $\tau=J$ is unchanged, those of the next two levels $\tau=J-1$ and $J-2$ change their signs, those of the next two $\tau=J-3$ and $J-4$ remain unchanged, etc. With respect to (b), the wave function of the lowest level $\tau=-J$ remains unchanged, those of the next two levels $\tau=-J+1$ and $-J+2$ change their signs, those of $\tau=-J+3$ and $-J+4$ remain unchanged, etc. On denoting the evenness and oddness of the wave functions by the + and the − sign respectively, we can represent the symmetry properties of the wave functions with respect to the operations (a) and (b) by the symbols (+ +), (+ −), (− +) or (− −).

The intensities of the pure rotational lines are determined by the matrix elements of the components of the permanent electric moment along the space axes x, y, z, namely,

$$\mathfrak{M}_x = \sum_{\xi} \int \overset{*}{\Psi}_{J\tau M}\ \mathfrak{M}_{\xi}\ \cos \widehat{\xi x}\ \Psi_{J'\tau'M'}\ d\tau \qquad (37)$$

the summation being over ξ, η, ζ. As the integrations are taken over all the values of the rotational coordinates., *i.e.*, the angles ϑ, φ, ψ, the vanishing or non-vanishing of the matrix elements can be determined from the properties of the integrands. Reference to Fig. 16 shows that the components of the electric moments possess the following evenness or oddness with respect to the above two operations (a) and (b):

$$\begin{array}{lcc}
 & \text{(a)} & \text{(b)} \\
\mathfrak{M}_\xi \cos \widehat{\xi x},\ \mathfrak{M}_\xi \cos \widehat{\xi y},\ \mathfrak{M}_\xi \cos \widehat{\xi z} & - & + \\
\mathfrak{M}_\eta \cos \widehat{\eta x},\ \mathfrak{M}_\eta \cos \widehat{\eta y},\ \mathfrak{M}_\eta \cos \widehat{\eta z} & - & - \\
\mathfrak{M}_\zeta \cos \widehat{\zeta x},\ \mathfrak{M}_\zeta \cos \widehat{\zeta y},\ \mathfrak{M}_\zeta \cos \widehat{\zeta z} & + & -
\end{array} \qquad (38)$$

Since the matrix elements in (37) do not vanish only if the integrands are even with respect to rotations of the molecule about the ζ and ξ axes through π, that is, with respect to the operations (a) and (b), the following selection rules are obtained on combining (38) with the symmetry properties of the wave functions of the rotational states:

(1) If the permanent electric moment is along the axis of least moment of inertia, only transitions between states are active in absorption, whose wave functions have the following properties with respect to the operations (a) and (b).

$$(+\ -) \longleftrightarrow (-\ -), \quad \text{or} \quad (+\ +) \longleftrightarrow (-\ +)$$

(2) If the permanent electric moment is along the axis of middle moment of inertia (η axis), only transitions between states $(+\ +) \longleftrightarrow (-\ -)$, or $(+\ -) \longleftrightarrow (-\ +)$ are active in absorption.

(3) If the permanent electric moment is along the axis of greatest moment of inertia (ζ axis), only transitions between states $(+\ +) \longleftrightarrow (+\ -)$ or $(-\ -) \longleftrightarrow (-\ +)$ are active in absorption.

(4) For all infrared active rotational lines, $\Delta J=0,\ \pm 1$.

These selection rules greatly limit the possibility of radiative transitions. Even then, however, the number of infrared active lines for a transition between two states J and $J+1$ is still very much greater than the number in the corresponding transition $J \rightarrow J+1$ in the symmetrical rotator. For example, the number of lines in the transitions $J=3, \tau$ to $J=4, \tau'$ of an asymmetrical rotator with the electric moment along the axis of middle moment of inertia is 16. In the case of the symmetrical rotator, the number of lines for the transitions $J=3$ to $J=4$ is only four according to (28) if the electric moment is along the axis of symmetry, and the number is 7 if the electric moment is perpendicular to the axis of symmetry (in a perpendicular vibration-rotational band, see the following section). For high values of J, the number of lines in the case of the asymmetrical rotator is enormous. Thus the spectrum of an asymmetrical rotator is very much more complicated than that of a symmetrical rotator.

The intensities of the individual lines $J, \tau - J', \tau'$ of an asymmetrical rotator are given by the formulae (11), (12) and (13) in which the matrix elements $\mathfrak{M}$ $(J, \tau; J', \tau')$ are more complicated functions of the quantum numbers than (15) and (30). We shall not go into the derivation of the expressions for the various matrix elements, not only because of their complexities, but also because of the fact that so far only in one or two case are the rotatoinal lines sufficiently well analyzed and their intensities measured to justify a comparison with the theoretical values. In general, because of the Boltzmann factor that would appear in the expression for the intensities as in (16) and (31), the intensities of lines arising from levels with high values of J are small, especially in molecules whose moments of inertia are small. In the case of the water molecule, it was found that practically all the observed lines in the rotational spectrum in the region between 80 cm^{-1} and 500 cm^{-1} can be accounted for by transitions between levels with J values below 11.[4] In heavy molecules, however, transitions involving levels with higher values of J may have considerable intensities and the observed spectra may be expected to be even richer in lines than the water vapor spectrum.

§2. Vibration-rotational Spectra

So far we have considered the vibration and the rotation of a molecule separately. When we consider the simultaneous vibration and rotation, we may in a first approximation assume that the energy of a molecule is the sum of the vibrational energy of a non-rotating molecule and the rotational energy of a rigid rotator, *i.e.*,

$$E = E_{vib} + E_{rot}, \tag{39}$$

and that the wave function is the product of the wave functions of the vibrator and the rotator

$$\Psi = \psi_{vib} \cdot \psi_{rot} = \psi_V \cdot \psi_R, \tag{40}$$

where V and R denote the totalities of the vibrational and the rotational quantum numbers respectively. The possibility of separating the energy of a rotating oscillator into E_{vib} and E_{rot} is not so obvious as it may seem, for the interactions between the vibrational and the rotational motions give rise to certain terms in the Hamiltonian function of the system that are not always small. It has been shown, however, by Eckart[1] and by Van Vleck[2] that a detailed treatment with the use of a properly chosen set of coordinates justifies the process of separation (39) and (40). In this section, we shall neglect these interactions and examine the spectrum of a molecule on the basis of (39) and (40).

With the energy of a molecule given by (39), one has only to consider the selection rules in order to obtain the spectrum of the molecule. For this purpose, it is necessary to examine the matrix elements of the components of the electric moment of the molecule along certain directions fixed in space. Consider a molecule in general (an asymmetrical rotator) and let a system of axes ξ, η, ζ be fixed in the molecule, their directions being along the principal axes of moment of inertia I_A, I_B, I_C respectively. The electric moment along the ξ axis, for example, is given by (31) of Chap. II, namely,

$$\mathfrak{M}_\xi = \overset{\circ}{\mathfrak{M}}_\xi + \sum_i \left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0 X_i + \cdots\cdots\cdots, \tag{41}$$

and the component of the electric moment along the direction of the x-axis, for example, is given by (32a) of Chap. II,

$$\mathfrak{M}_x = \sum \overset{\circ}{\mathfrak{M}}_\xi \cos \widehat{\xi x} + \sum_\xi \sum_i \left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0 X_i \cos \widehat{\xi x}, \tag{42}$$

in which the summation in ξ is taken over ξ, η, ζ. The matrix element of $\mathfrak{M}_x$ associated with the transition V, R→V', R' is given by

$$\begin{aligned}\mathfrak{M}_x(V,R;\,V',R') = {} & \sum_\xi \overset{\circ}{\mathfrak{M}}_\xi\, \mathfrak{a}_{\xi x}(R;\,R') \cdot \delta(V,\,V') \\ & + \sum_\xi \sum_i \left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0 X_i(V;\,V') \cdot \mathfrak{a}_{\xi x}(R,\,R'),\end{aligned} \tag{43}$$

where

$$X_i(V;\,V') = \int \overset{*}{\psi}_V\, X_i\, \psi_{V'}\, d\tau, \tag{44}$$

and

$$\mathfrak{a}_{\xi x}(R;\,R') = \int \overset{*}{\psi}_R \cos \widehat{\xi x}\; \psi_{R'}\, d\sigma. \tag{45}$$

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[1] C. Eckart, Phys. Rev. 46, 383, (1934); 47, 552, (1935).

[2] J. H. Van Vleck, Phys. Rev. 47, 487, (1935).

$\alpha_{\xi x}(R;R')$ is the matrix element of the direction cosine cos $\widehat{\xi x}$ associated with the rotational states R and R'. When there is no change in the vibrational state, *i.e.*, $V=V'$, the second term in (43) vanishes on account of (63) of Chap. III and the first term simply gives the selection rules for the pure rotational spectrum which we have already considered in the last section. In a transition involving a change in the vibrational state, the first term in (43) vanishes and (43) reduces to

$$\mathfrak{M}_x(V,R;V',R') = \sum_{\xi}\sum_{i}\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0 X_i(V;V')\cdot\alpha_{\xi x}(R;R'). \tag{43a}$$

Entirely similar expressions hold for $\mathfrak{M}_y(V,R;V',R')$ and $\mathfrak{M}_z(V,R;V',R')$. Hence the selection rules are determined by the factors $\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0$, $X_i(V;V')$ and $\alpha_{\xi x}(R;R')$ for $\xi=\xi,\eta,\zeta$.

A) Consider first the linear rotator. If in the transition of the vibrational state $V_i\to V_i+1$ the change of the electric moment lies in the direction of the symmetry axis, *i.e.*, $\left(\frac{\partial \mathfrak{M}_\zeta}{\partial X_i}\right)_0\neq 0$, then the matrix elements of $\mathfrak{M}_x,\mathfrak{M}_y,\mathfrak{M}_z$ will not all vanish if $\alpha_{\zeta x}(R;R')$, $\alpha_{\zeta y}(R;R')$ and $\alpha_{\zeta z}(R;R')$ do not all vanish. But the condition for this is just that given by (9), namely,

$$\Delta J=\pm 1 \qquad \Delta m = 0,\pm 1. \tag{46}$$

Such a band is called a "parallel" type band.

If in the transition $V_i\to V_i+1$ the electric moment changes in directions perpendicular to the symmetry axis, *i.e.*, $\left(\frac{\partial \mathfrak{M}_\xi}{\partial X_i}\right)_0\neq 0$, $\left(\frac{\partial \mathfrak{M}_\eta}{\partial X_i}\right)\neq 0$, then the matrix elements of $\mathfrak{M}_x,\mathfrak{M}_y,\mathfrak{M}_z$ will not all vanish if $\alpha_{\xi x}(R;R')$, ...$\alpha_{\xi z}(R;R')$,.......$\alpha_{\eta z}(R;R')$ do not all vanish. A detailed examination shows that in this case, in addition to those allowed by (46), transitions $\Delta J=0$ are also allowed. Such a band is called a "perpendicular" type band. The appearance of these two types of bands can be obtained from the selections and the energy expression (4).

"Parallel" bands $\Delta J=\pm 1$

Positive or R branch $(J\to J+1)$: $\nu=\nu_0+\frac{h}{4\pi^2 I}(J+1)$

Negative or P branch $(J+1\to J)$: $\nu=\nu_0-\frac{h}{4\pi^2 I}(J+1)$ (47)

"Perpendicular" bands $\Delta J = 0, \pm 1$

Positive or R branch $(J \rightarrow J+1)$: $\nu = \nu_0 + \frac{h}{4\pi^2 I}(J+1)$

Zero or Q branch $(J \rightarrow J)$: $\nu - \nu_0$

Negative or P branch $(J+1 \rightarrow J)$: $\nu = \nu_0 - \frac{h}{4\pi^2 I}(J+1)$ (,8)

where ν_0 is the frequency of the transition of the vibrational state alone, *i.e.*, $h\nu_0 = E_{v+1} - E_v$. Thus a perpendicular band of a linear molecule differs from a parallel band in the presence of a Q branch in the former, which consists of a large number of lines falling on one another. This exact coincidence of the lines in the Q branch corresponding to various transitions $J \rightarrow J$, and the equidistant spacing of the lines in the R and the P branches result from our neglect of the interactions between the vibrational and the rotational motions of the molecule, but would be destroyed when they are taken into account. This will be discussed in §4 of this chapter.

It is seen that the results obtained with the quantum theory above agree in the main with those of the classical theory (Chap. II, section 4), except that the continuous distribution of the rotational frequencies according to the latter is now replaced by a discrete structure.

The intensities of the rotational lines in the R branch of a parallel band are given by the equations (11), (12) and (13) in which ν is given by (47). The intensities of the P branch lines can be obtained from (11), (12) and (13) by a proper change of the quantum numbers J and J+1 appearing in them.

B) For a symmetrical rotator, if the electric moment changes during the vibration along the symmetry axis, the selection rules are given by the condition that the matrix elements of $\cos \widehat{\zeta x}$, $\cos \widehat{\zeta y}$, $\cos \widehat{\zeta z}$ do not all vanish. This is seen to be the same as (28), namely,

$$\Delta J = 0, \pm 1; \qquad \Delta K = 0; \qquad \Delta M = 0 \pm 1, \tag{49}$$

Such a band is called a "parallel" type band.

If in the vibration the electric moment changes in directions perpendicular to the symmetry axis, say along the ξ-axis in Fig. 16, one has to consider the matrix elements of the components of the electric moment

$$\mathfrak{M}_z = \mathfrak{M}_\xi \sin\varphi \sin\vartheta; \qquad \mathfrak{M}_x \pm i\mathfrak{M}_y = \mathfrak{M}_\xi (\cos\varphi \pm i \sin\varphi \cos\vartheta)\, e^{\pm i\psi}\,.$$

A little consideration shows that the selection rules for J and M are the same as in (49), but because of the factors *sin* φ and *cos* φ, the selection rule for K is now $\Delta K = \pm 1$. Hence one obtains

$$\Delta J = 0, \pm 1; \qquad \Delta K = \pm 1; \qquad \Delta M = 0, \pm 1. \tag{50}$$

Such a band is called a "perpendicular" type band.

The structure of the parallel and the perpendicular type bands can be obtained from the selection rules (49) and (50) and the energy expression (25).

1) "Parallel" bands $\Delta J = 0, \pm 1; \quad \Delta K = 0; \quad \Delta M = 0, \pm 1$

$$\begin{aligned} &\text{Positive or } R \text{ branch} (J \rightarrow J+1): && \nu = \nu_0 + \frac{h}{4\pi^2 I_A}(J+1) \\ &\text{Zero or } Q \text{ branch} \quad (J \rightarrow J): && \nu = \nu_0 \\ &\text{Negative or } P \text{ branch} (J+1 \rightarrow J): && \nu = \nu_0 - \frac{h}{4\pi^2 I_A}(J+1). \end{aligned} \tag{51}$$

The intensities of the various transitions are given by

$$R \text{ branch}: I(J \rightarrow J+1) = A \sum_{-J}^{J}{}_K \frac{(J+1)^2 - K^2}{(J+1)} e^{-\alpha J(J+1) - \alpha\beta K^2}$$

$$Q \text{ branch}: I(J \rightarrow J) = A \sum_{J=0}^{\infty} \sum_{-J}^{J}{}_K \frac{K^2(2J+1)}{J(J+1)} e^{-\alpha J(J+1) - \alpha\beta K^2}$$

$$P \text{ branch}: I(J+1 \rightarrow J) = e^{-2\alpha(J+1)} J(J \rightarrow J+1) \tag{52}$$

where

$$A = \frac{8\pi^3 N\nu}{3(\Sigma g_{JK}\, e^{-\frac{E}{kThc}})} \left| \left(\frac{\partial \mathfrak{M}_\zeta}{\partial X_i}\right)_0 X_i(\acute{v}; v') \right|^2 \left(1 - e^{-\frac{h\nu}{kT}}\right), \tag{53}$$

and ν is given by equations (51) for the corresponding expressions in (52), but can be given the value ν_0 since ν_0 is in general large compared with $\frac{h}{4\pi^2 I_A}(J+1)$. The general appearance of the parallel type band is similar to that of a linear molecule, but with the addition of a Q branch. When observed with a spectrometer with low dispersion so that the rotational lines are not resolved, the envelope presents a doublet structure with an intense Q branch. The separation between the intensity maxima of the doublet depends on the moments of inertia and the temperature of the absorbing gas, as can be seen from (52).

Qualitatively, the greater the moments of inertia of the molecule, the smaller will be this separation.

2) "Perpendicular" bands $\Delta J=0, \pm 1$; $\Delta K=\pm 1$; $\Delta M=0, \pm 1$

The structure of a perpendicular type band is much more complicated than that of a parallel band because of the many possible transitions $K \rightarrow K \pm 1$ for a given transition $\Delta J=0, \pm 1$. Consider first the transitions in which $K+1 \rightarrow K$. The frequencies of the band lines are given by

$$\begin{aligned} &R \text{ branch } (J \rightarrow J+1): && \nu = \nu_0 + \frac{h}{4\pi^2 I_A}\left[(J+1) - \beta\left(K+\tfrac{1}{2}\right)\right] \\ &Q \text{ branch } (J \rightarrow J) \quad : && \nu = \nu_0 - \frac{h}{4\pi^2 I_A}\,\beta\left(K+\tfrac{1}{2}\right) \qquad (54) \\ &P \text{ branch } (J+1 \rightarrow J): && \nu = \nu_0 + \frac{h}{4\pi^2 I_A}\left[-(J+1) - \beta\left(K+\tfrac{1}{2}\right)\right]. \end{aligned}$$

For each given value of K, equations (54) represent a band similar to the parallel band (51), but displaced bodily to the low frequency side by $\frac{h}{4\pi^2 I_A}\beta\ (K+\frac{1}{2})$, where β is given by (26), and with this further difference: Since $|K| \leqq J$, the first line $J \rightarrow J+1$ in the R branch arises from $J=K+1$ while the first line $J+1 \rightarrow J$ in the P branch arises from $J=K$. Thus $K+1$ lines in the R branch and K lines in the P branch are missing near the center of this band.

For transitions in which $K \rightarrow K+1$, one obtains, corresponding to (54),

$$\begin{aligned} &R \text{ branch } (J \rightarrow J+1): && \nu = \nu_0 + \frac{h}{4\pi^2 I_A}\left[(J+1) + \beta\left(K+\tfrac{1}{2}\right)\right] \\ &Q \text{ branch } (J \rightarrow J) \quad : && \nu = \nu_0 + \frac{h}{4\pi^2 I_A} \cdot \beta\left(K+\tfrac{1}{2}\right) \qquad (55) \\ &P \text{ branch } (J+1 \rightarrow J): && \nu = \nu_0 + \frac{h}{4\pi^2 I_A}\left[-(J+1) + \beta\left(K+\tfrac{1}{2}\right)\right]. \end{aligned}$$

These again represent a parallel type band displaced bodily to the high frequency side of ν_0 by $\frac{h}{4\pi^2 I_A}\beta\ (K+\frac{1}{2})$, with the first K lines in the R branch and the $K+1$ lines in the P branch missing.

The whole perpendicular band consists of the totality of all the bands represented by (54) and (55) for all values of K, as shown in

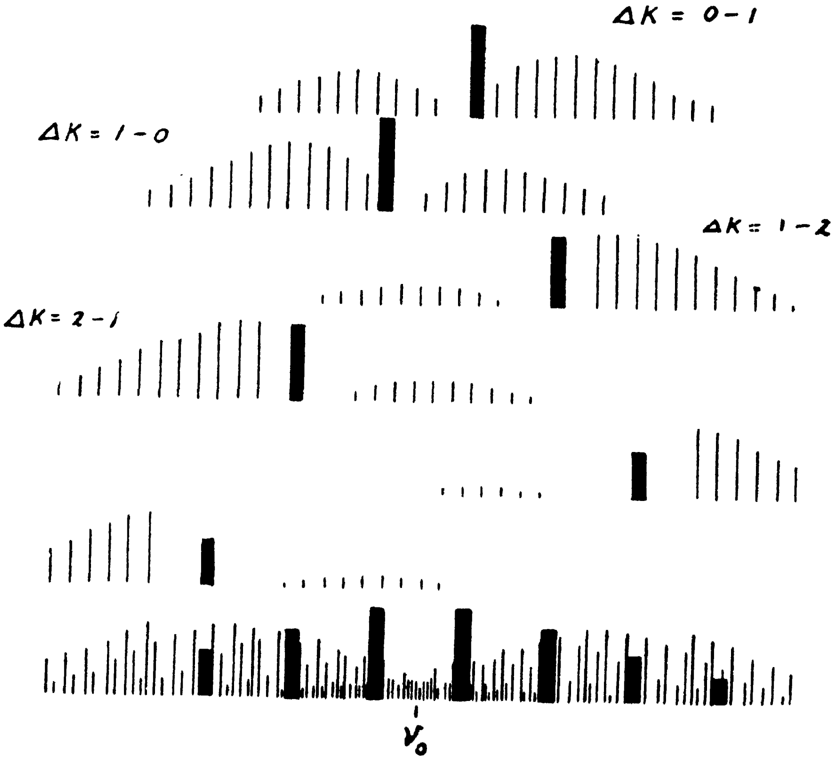

Fig. 18. Perpendicular type band of a symmetrical rotator.

Fig. 18. Since the component bands (54) and (55) are placed at the interval $\beta\,(h/4\pi^2 I_A)$, the rotational lines of the various bands in general will not fall on one another, unless β happens to be an exact integer. Even then the effect of the interactions between the vibration and the rotation of the molecule will destroy the exact coincidence of the lines of the different component bands. Since the number of lines in the whole band is infinite (of course lines originating from levels of high values of J and K have low intensities on account of the Boltzmann factor), the absorption spectrum will be practically continuous with the Q branches of the component bands protruding more or less prominantly from the background. This is especially so when the band is observed with a spectrometer of only moderate dispersion.

The intensities of the rotational lines given by (54) and (55) are given by the expressions

$$R \text{ branch: } I(J,K+1 \rightarrow J+1,K) = A\frac{(J-K)(J-K+1)}{2(J+1)}e^{-\alpha J(J+1)-\alpha\beta(K+1)^2}$$

$$Q \text{ branch: } I(J,K+1 \rightarrow J,K)$$

$$= A \overset{\infty}{\underset{K}{\Sigma}}{}_{J} \frac{(2J+1)(J-K)(J+K+1)}{2J(J+1)} e^{-\alpha J(J+1)-\alpha\beta(K+1)^2} \qquad (56)$$

$$P \text{ branch: } I(J+1,K+1 \rightarrow J,K)$$

$$= A\frac{(J+K+1)(J+K+2)}{2(J+1)} e^{-\alpha(J+1)(J+2)-\alpha\beta(K+1)^2}$$

$$R \text{ branch: } I(J,K \rightarrow J+1,K+1) = A\frac{(J+K+1)(J+K+2)}{2(J+1)}e^{-\alpha J(J+1)-\alpha\beta K^2}$$

$$Q \text{ branch: } I(J,K \rightarrow J,K+1)$$

$$= A \overset{\infty}{\underset{K}{\Sigma}}{}_{J} \frac{(2J+1)(J-K)(J+K+1)}{2J(J+1)} e^{-\alpha J(J+1)-\alpha\beta K^2} \qquad (57)$$

$$P \text{ branch: } I(J+1,K \rightarrow J,K+1) = A\frac{(J-K)(J-K+1)}{2(J+1)}e^{-\alpha(J+1)(J+2)-\alpha\beta K^2}$$

where A is given by an expression similar to (53).

With these expressions for the intensities, Gerhard and Dennison[1] have calculated the envelopes of the perpendicular bands of symmetrical rotators as a function of the parameter $\beta = \frac{I_A}{I_C} - 1$, the assumption being made that the moment of inertia I_A is not too small so that the summations can be approximated by integrations. The forms of the envelopes for a few values of β are shown in Fig. 19. It is seen how strongly the general appearance of a perpendicular band depends on the values of the principal moments of inertia of the molecule. These authors have also shown how to obtain an estimate of the parameter β from (i) the ratio of the intensity of the Q branch to the total intensity of the whole band, and (ii) the separation of the intensity maxima in the two outer branches as compared with the separation in the parallel type bands of the same molecule, which is indicated by the two vertical lines under each curve. Although this method of Gerhard and Dennison is only approximate and holds only for molecules whose moments of inertia are not too small, nevertheless it furnishes an extremely useful criterion for the classification of the observed bands of a molecule and provides a check for the values of the moments of inertia obtained by other methods.

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[1] S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197, (1933).

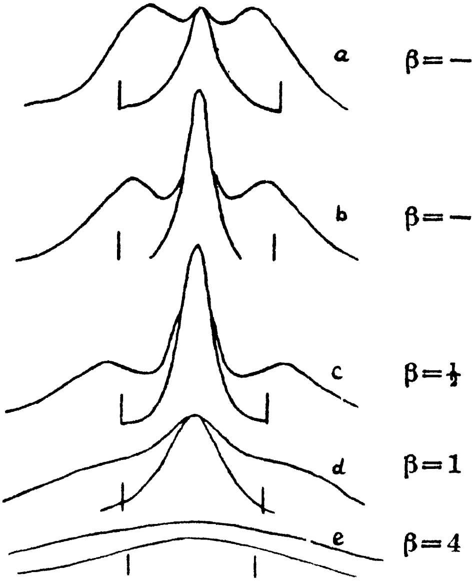

Fig. 19. Envelopes of perpendicular type bands of symmetrical rotators. (a) $\beta = -\frac{1}{2}$ or $I_A = \frac{1}{2} I_C$. This corresponds to disk like molecules; (b) $\beta = -\frac{1}{3}$ or $I_A = \frac{2}{3} I_C$; (c) $\beta = \frac{1}{2}$ or $I_A = \frac{3}{2} I_C$; (d) $\beta = 1$ or $I_A = 2 I_C$; (e) $\beta = 4$ or $I_A = 5 I_C$.

C) The vibration-rotational bands of an asymmetrical rotator possess even more complicated structures than the perpendicular type bands of the symmetrical rotator. The energy of vibration and rotation is given by (39) in which E_{rot} is given by (35). The selection rules are given by (43a). It is seen from (43) that, since the matrix elements of the components of the electric moment in the pure rotational spectrum and in the vibration-rotational spectrum depend in the same way on the rotational quantum numbers R and R' through the matrix elements $\alpha_{\xi x}(R; R')$, $\xi=\xi, \eta, \zeta$, $x=x, y, z$, the selection rules for the vibration-rotational lines must be the same as those for the pure rotational lines. These selection rules have been given in §1, C) of this chapter.

The detailed structure of a vibration-rotational band is determined by (1) the values of the principal moments of inertia which determine the positions of the energy levels and also the intensities of the various allowed transitions through the Boltzmann factors, and (2) the direction of the change of the electric moment during the vibration, which determines the selection rules and hence the pattern of the band. Dennison[1] has calculated the rotational lines involing levels J up to 4 of a planar asymmetrical rotator, $I_A+I_B=I_C$, for values of $\varrho=I_A/I_B$ from 0.10 to 1.0, for both cases in which the electric moment changes along the axes of I_A and I_B. While the calculated patterns are already very complicated and will be even more so when transitions involving higher values of J are included (as it must be done in the case of molecules whose moments of inertia are not small), the following qualitative statements can be made:

(1) If the change of the electric moment is along the axis of least moment of inertia I_A (type A band), there is an accumulation of lines (arising from transitions $J, \tau \rightarrow J, \tau'$) near the center of the band, giving the appearance of a Q branch which is the sharper the smaller the value $\varrho=I_A/I_B$. For very small values of ϱ, *i.e.*, for a rotator which is only slightly asymmetrical, Nielsen[2] has calculated the rotational structure and found that it is similar to the parallel band of a symmetrical rotator, but with the Q branch and each individual line $J \rightarrow J \pm 1$ split into a number of lines. For $\varrho < 0.1$, the splittings are small and the separations between these groups of fine structure lines are approximately given by $\frac{h}{8\pi^2 I_C}$. This result can be easily understood from Fig. 17 and the perturbation method for the calculation of the energies of a slightly asymmetrical rotator. Certain bands of such molecules as formaldehyde OCH_2 and ethylene C_2H_2 when observed with very high dispersion and resolution should exhibit this fine structure of each rotational "line". A calculation shows, however, that the moments of in-

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[1] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

[2] H. H. Nielsen, Phys. Rev. 38, 1432, (1931).

ertia of these molecules are such that experimentally it is very difficult to observe these splittings.

(2) If the change of the electric moment is along the axis of the middle moment of inertia I_B (type *B* band), the rotational lines gather on the two sides of the band center ν_0, producing an apparent gap at the center. It is seen that in the limit $\varrho=1$, both the *A* and the *B* type bands reduce to the perpendicular type band of a symmetrical rotator, with $I_A=I_B=\frac{1}{2}I_C$. According to (54) and (55), such a band consists of a number of lines (each of which in turn consists of a number of coincident lines) at distances $\pm\frac{h}{8\pi^2 I_C}(\frac{1}{2}+n)$ from the center, where $n=0, 1, 2, 3 \ldots\ldots$

(3) If the change of the electric moment is along the axis of greatest moment of inertia I_C (type *C* band), there is again an accumulation of lines near the center of the band, giving the appearance of a strong "Q" branch. In the limit of $I_A=I_B$, the structure reduces to that of the parallel type band of a symmetrical rotator (a disk-like molecule). The rotational structure for very small values of ϱ for plane molecules has also been calculated by Nielsen.

Very recently, Badger and Zumwalt[3] have calculated the band envelopes of these three types of bands in the same way as Gerhard and Dennison have done for the symmetrical rotators. The asymmetry of the molecules is given by two parameters $S=\left(\frac{2}{I_B}-\frac{1}{I_A}-\frac{1}{I_C}\right)\Big/\left(\frac{1}{I_A}-\frac{1}{I_C}\right)$ and $\varrho=I_B\left(\frac{1}{I_A}-\frac{1}{I_C}\right)$. In the limiting cases of (*i*) a planar molecule ($I_C=I_A+I_B$), (*ii*) a symmetrical disk-like molecule ($I_C=2I_A$), and (*iii*) a symmetrical long cylindrical molecule ($I_B=I_C$), the values of these parameters are (*i*) $S=2\left(\frac{I_A}{I_B}\right)^2-1$, $\varrho=I_B^2/I_A(I_A+I_B)$ (*ii*) $S=1$, $\varrho=\frac{1}{2}$, (*iii*) $S=-1$, $\varrho=\left(\frac{I_B}{I_A}\right)-1$ respectively. The results for a few values of ϱ for $S=-\frac{1}{2}$, 0, $\frac{1}{2}$ are given in Fig. 20. With spectrometers of moderate or even high resolution, it is only these band envelopes that are usually observed, except in the case of a few molecules whose moments of inertia are small, like H_2O and H_2S. It is seen that the marked difference in the envelopes of these different types of bands is extremely useful in the classification of the observed bands of a molecule.

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[3] R. M. Badger and L. R. Zumwalt, Jour. Chem. Phys. 6, 711, (1938).

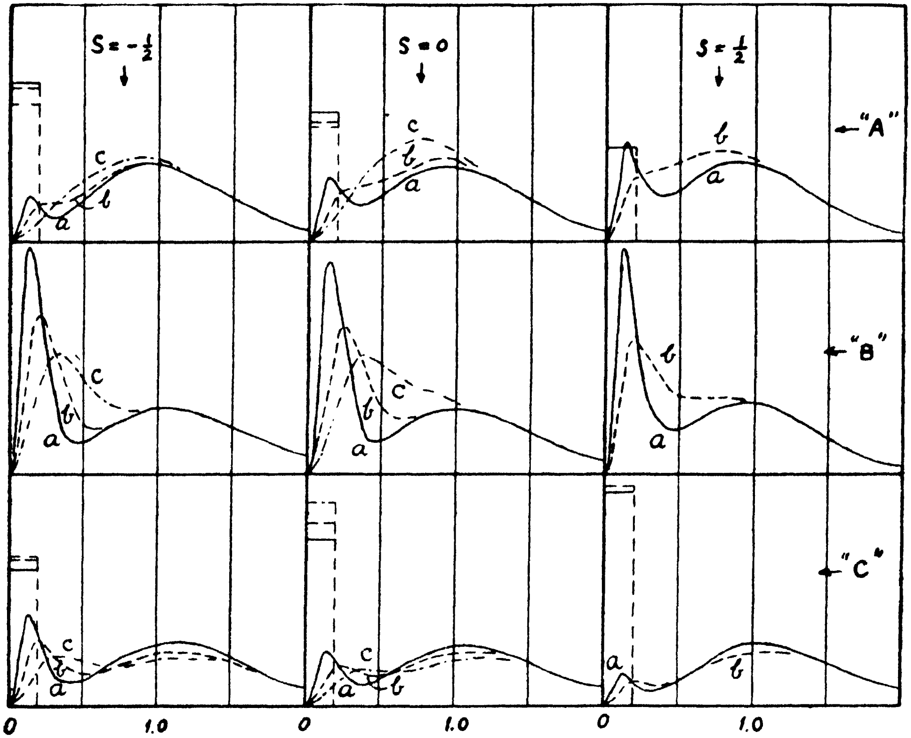

Fig. 20. Envelopes of "A," "B," "C" type vibration-rotational bands of asymmetrical rotators. Ordinates are absorption coefficients; abscissa are in units of $x=(\nu-\nu_0)\pi(2B/kT)^{\frac{1}{2}}$. (a) curves in solid lines, $\rho=\frac{1}{8}$; (b) curves in dashed lines, $\rho=\frac{1}{2}$; (c) curves in dote and dashes, $\rho=\frac{1}{4}$. Rectangles indicate the total intensities of the Q branches. Only one half of each band is shown.

§3. Nuclear Spins and Intensities of Rotational Lines

In the last section, we have obtained the intensities of the rotational lines in the vibration-rotational bands of a molecule from considerations of the matrix elements of the electric moment for various transitions, and the statistical weights of the various states; that is, from considerations of the vibrational and rotational wave functions alone. In addition to these, however, the complete wave function of a molecule contains a part for the electronic motions and another part for the nuclear spins of the atoms in the molecule. In this section, we shall indicate how the inclusion of the spins of the nuclei may affect the intensity and the selection rules in the spectrum of a molecule, and shall only treat the case of the linear symmetrical YX_2 molecule as an example. For other important molecular models such as the triangular YX_2, planar

YX_3 and axially symmetrical YX_3 and ZYX_3 and tetrahedral YX_4, we shall again refer the reader to the work of Dennison[1] on which the following is based.

Consider a system of particles, an atom or a molecule, of which two, say, are identical. The wave function of the system ψ must be such that

$$\int \overset{*}{\psi}\,\psi\,d\tau = 1, \tag{58}$$

in which the integration is taken over all possible values of the coordinates of all the particles in the system. If the two identical particles, denoted simply as 1 and 2, be interchanged, the value of the integral (58) must evidently remain unchanged, since $\overset{*}{\psi}\psi\,d\tau$, which gives the probability of finding the system in the volume element $d\tau$, is not changed by interchanging two particles that are identical. There are two possibilities, however, for the behavior of the wave function ψ towards such an interchange, that leave the integral (58) unchanged, namely, the wave function ψ may either remain unchanged, or merely change its sign upon the interchange of the two identical particles,

$$\begin{aligned} \psi_s(1, 2) &= \psi_s(2, 1), \\ \psi_a(1, 2) &= -\psi_a(2, 1). \end{aligned} \tag{59}$$

In the first case, the wave function is said to be symmetrical with respect to the two particles and in the second case antisymmetrical. Since both classes of these wave functions answer the requirement of leaving (58) invariant, it seems that they may both be employed for the description of the state of the system. It can be shown, however, that no physical quantities may have a non-vanishing matrix element connecting states whose wave functions belong to different classes.[2] Hence if both classes of wave functions do exist, they must be independent of each other. A profound hypothesis in the quantum mechanics states, however, that in

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[1] D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

[2] For consider any physical quantity F of the system. As such, it must remain unchanged upon the interchange of two ideneical particles, *i.e.*, $F(1, 2) = F(2, 1)$. Now on interchanging the two particles, the matrix element of F

$$\int \overset{*}{\psi}_s\,F\,\psi_a\,d\tau$$

must remain unchanged since interchanging 1 and 2 simply amounts to a change of the names of the variables of integration. But as the antisymmetrical function ψ_a goes into its negative upon this interchange, the valuc of the integral must also change its sign upon this interchange. It follows that the integral can only be zero.

nature only one class of wave functions exists, which is of the antisymmetrical class for elementary particles like electrons and protons (which obey the Fermi-Dirac statistics) but is of the symmetrical class for particles like the helium nuclei which obey the Bose-Einstein statistics. In the case of the electrons in an atom, this hypothesis is equivalent to the Pauli Exclusion Principle which is fundamental in the theory of the structure of atoms.

Now in a molecule the energies associated with electronic, vibrational, rotational motions and the nuclear spins are such that

$$E_e >> E_v >> E_r >> E_s. \tag{60}$$

Because of this, the Schrödinger equation of the whole molecule may be solved in a first approximation by assuming the wave function to be a product of the electronic, vibrational, rotational and the nuclear spin wave functions each of which is a function of the respective coordinates

$$\Psi = \psi_e \cdot \psi_v \cdot \psi_r \cdot S_{m_s} \tag{61}$$

The requirement that the total wave function of the system be antisymmetrical with respect to the interchange of two atoms can be met by the following eight possibilities for the symmetry properties of the individual wave functions.

	electronic	vibrational	rotational	nuclear spin	
(1)	*s*	*s*	*a*	*s*	
(2)	*s*	*a*	*s*	*s*	
(3)	*a*	*s*	*s*	*s*	
(4)	*a*	*a*	*a*	*s*	(62s)
(5)	*s*	*s*	*s*	*a*	
(6)	*s*	*a*	*a*	*a*	
(7)	*a*	*s*	*a*	*a*	
(8)	*a*	*a*	*s*	*a*	(62a)

where *s* under the heading "electronic" means that the electronic part of the wave function is symmetrical with respect to the interchange of the two identical particles, etc. In the first four classes of wave functions (62s), the nuclear spin part is symmetrical with respect to the interchange, while in the second four classes (62a), it is antisymmetrical.

We can now show that no radiative transitions can take place between two states whose wave functions belong to (62s) and (62a) groups. Consider the matrix elements of the electric moment of the system. As the electric moment can not depend on the spins of the atomic nuclei (or more exactly speaking, it can only depend very slightly on the nuclear spins), it follows that the matrix element contains the integral $\int S_s S_a \, d\sigma_1 \, d\sigma_2$ as a factor, which vanishes for the same reason as given before.[3]

When we confine ourselves to the vibration-rotational spectrum of a molecule arising from transitions involving changes only in the vibrational and the rotational states but not in the electronic states, we have only to consider the following possibilities in the transitions:

$$\begin{array}{cccc}
(1) \longleftrightarrow (1) & (3) \longleftrightarrow (3) & (5) \longleftrightarrow (5) & (7) \longleftrightarrow (7) \\
(1) \longleftrightarrow (2) & (3) \longleftrightarrow (4) & (5) \longleftrightarrow (6) & (7) \longleftrightarrow (8) \\
(2) \longleftrightarrow (2) & (4) \longleftrightarrow (4) & (6) \longleftrightarrow (6) & (8) \longleftrightarrow (8)
\end{array} \qquad (63)$$

namely, transitions between states whose wave functions have the same symmetry character in the vibrational and rotational parts combined together, and the same symmetry character in the electronic and the nuclear spin parts separately.

The above results can be readily generalized to systems containing any number of identical particles. The effect of these considerations on the spectrum of a molecule may perhaps be best made clear by the following example.

Consider a symmetrical linear molecule YX_2. For the vibrational motions, we shall employ the coordinates σ, ϱ, ξ defined in (81) of Chap. III. As the degenerate vibration ν_2 is equivalent to a rotation of the Y and the two X atoms about a line parallel to the X-X line and going through the center of gravity of the molecule, we may in an approximation regard the molecule as a symmetrical rotator and introduce the Euler's angles ϑ, ψ, φ as shown in Fig. 21. The coordinate

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[3] This obtains because the effect of the nuclear spins is exceedingly small since the nuclear magnetic moments are in general of the order of a few thousandths of a Bohr magneton. In a system containing two electrons like the helium atom, the two classes of wave functions with their spin parts symmetrical and antisymmetrical correspond to two classes of non-combining states, namely, the triplet and the singlet states respectively. In the case of such heavy atoms as mercury, it is found that there are transitions between the singlet and the triple states. This is due to the fact that in such heavy atoms, the spin-orbit interactions (as represented by the multiplet splittings) are quite large, in fact they are of the same order of magnitude as the interactions between the two electrons (as represented by the singlet-triplet separations). In molecules, however, no transitions between states with wave functions differing in the symmetry properties in their spin parts may arise, since the effect of the nuclear spins is always small.

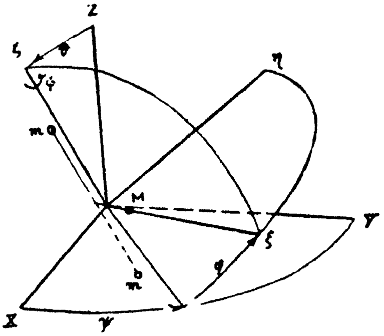

Fig. 21. Rotational coordinates of symmetrical YX_2 molecule

axes ξ, η, ζ are so chosen that ζ is along a line parallel to the X_2 line and ξ perpendicular to this line and going through the Y atom, the origin being at the c.g. of the molecule. The angle φ measures the angle of rotation about the ζ axis, and is hence identical with the angle φ introduced in Section 1, C and also (80) of Chap. III. The vibrational and rotational wave functions are, according to (82) of Chap. III and (18), (21) of this chapter,

$$\psi_{v_1}(\sigma)\cdot\psi_{v_2l}(\varrho)\cdot\psi_{v_3}(\xi)\sin^d\frac{\vartheta}{2}\cos^s\frac{\vartheta}{2}F(\sin^2\frac{\vartheta}{2})\cdot e^{il\varphi}\,e^{iM\psi}\,. \tag{64}$$

The symmetry properties of these wave functions with respect to the interchange of the two X atoms can be ascertained on the following considerations: Interchanging the two X atoms is brought about by a rotation of the ξ, η, ζ system about the ξ-axis through π. Remembering the meanings of the Euler's angles,[4] one can easily verify that the rotation about ξ through π changes the Euler's angles ϑ into $\pi-\vartheta$, ψ into $\psi+\pi$, and φ into $\pi-\varphi$. The wave functions $\psi_{v_1}(\sigma)$ and $\psi_{v_2l}(\varrho)$ are sysmetrical with respect to the interchange for all values of v_1 and v_2, since these vibrations are symmetrical with respect to the ξ-axis and reversing the direction of the X-X line leaves the system unchanged. The wave function $\psi_{v_3}(\xi)$ is symmetrical (or antisymmetrical) with respect to the interchange of the X atoms for v_3 even (or odd) on account of the properties of the Hermitian function and the fact that the coördinate ξ changes sign upon reversing the direction of the X-X line. For the rotational wave functions, let us first consider those levels with $l=0$. Then according to (21), $d=s=M$, and upon the above changes of the Euler's angles,

$$\sin^M\left(\frac{\pi}{2}-\frac{\vartheta}{2}\right)\cos^M\left(\frac{\pi}{2}-\frac{\vartheta}{2}\right)e^{iM(\psi+\pi)}$$

$$=\pm\sin^M\frac{\vartheta}{2}\cos^M\frac{\vartheta}{2}\,e^{iM\psi}\quad\text{for } M\begin{cases}\text{even}\\\text{odd}\end{cases}. \tag{65}$$

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[4] A rotation about the space z-axis through ψ brings the space x-axis into coincidence with the K-axis, the intersection between the $\xi-\eta$ and the x-y planes. A rotation now about K through ϑ brings the z-axis into coincidence with the ζ-axis. Finally a rotation about the ζ-axis through φ brings the x-axis into coincidence with the ξ-axis and hence the y-axis with the η-axis simultaneously.

It can be shown from the expression (24) for $F(t)=F\left(\sin^2\frac{\vartheta}{2}\right)$ and (23), (27) that

$$F\left(\cos^2\frac{\vartheta}{2}\right)=\pm F\left(\sin^2\frac{\vartheta}{2}\right) \quad \text{for } J-M=\begin{cases}\text{even}\\ \text{odd}\end{cases} \tag{66}$$

Hence for states $l=0$, the total rotational wave function is symmetrical and antisymmetrical with respect to the interchange of the X atoms for $J=$ even and odd respectively.

For states with $l\neq0$, each rotational level is doubly degenerate. One may form the combinations $\frac{1}{\sqrt{2}}\left(e^{il\varphi}\pm e^{-il\varphi}\right)$. Upon the change $\varphi\rightarrow\pi-\varphi$, one of these wave functions is symmetrical and the other is antisymmetrical. Similar arguments as above hold for the parts depending on ϑ and ψ. Hence for $l\neq0$, each level consists in fact of a pair of coincident levels, one with symmetrical and one with antisymmetrical rotational wave function.

Now let us consider the nuclear spin wave functions. If the nucleus of the X atoms possesses a spin angular momentum s (in units of $h/2\pi$), then its component along a certain direction in space (say, a preferential direction furnished by an external magnetic field) may take on $2s+1$ values M_s for each of which there is one spin wave function S_{M_s}. For two X atoms there are $(2s+1)^2$ wave functions $S_{M_{si}}(\sigma_1)$ $S_{M_{sj}}(\sigma_2)$. Of these there are $2s+1$ for which $M_{si}=M_{sj}$ and hence they are symmetrical with respect to the interchange of the X atoms. The rest $2s(2s+1)$ wave functions can be grouped in pairs in the form $S_{M_{si}}(\sigma_1)S_{M_{sj}}(\sigma_2)$ and $S_{M_{si}}(\sigma_2)S_{M_{sj}}(\sigma_1)$. In the approximation in which the interaction between the nuclear spins is neglected, these two wave functions correspond to the same energy of the molecule and hence the state is degenerate. This degeneracy is removed by taking into consideration the interaction between the nuclear spins, and the correct wave functions are then the combinations $\frac{1}{\sqrt{2}}\left[S_{M_{si}}(\sigma_1)\,S_{M_{sj}}(\sigma_2)\pm S_{M_{si}}(\sigma_2)\,S_{M_{sj}}(\sigma_1)\right]$. Of these the $s(2s+1)$ with the $+$ sign are symmetrical and the $s(2s+1)$ with the negative sign are antisymmetrical with respect to the interchange. Hence there are altogether $(s+1)(2s+1)$ symmetrical and $s(2s+1)$ antisymmetrical spin wave functions. Since the splittings of the energy levels due to the spin interactions are too small to reveal themselves in the spectrum, for all purposes we may regard all the levels as coincident, their statistical weights due to the spin degeneracy being given by $(s+1)(2s+1)$ and $s(2s+1)$.

We are now in a position to obtain the intensities of the rotational lines of the various vibration-rotational bands of the linear symmetrical YX_2 molecule. First consider the fundamental bands. The transition v_1, v_2, $v_3=0,0,0$ to $1,0,0$ has zero intensity as the change of the electric moment during the vibration ν_1 is zero. In the transition $0,0,0 \rightarrow 0,1,0$ so that $l=0$ and $l'=1$, the symmetry characters of the rotation levels in the upper and the lower vibratinal states are as shown in Fig. 22 in which levels differing in symmetry properties in the spin parts of their wave functions are represented by solid and dotted lines.

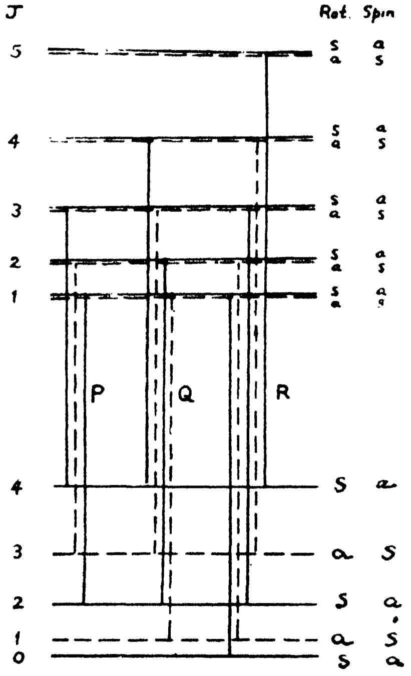

Fig. 22. Rotational structure of ν_2 band of linear YX_2

Let us assume, for the sake of definiteness, that the total wave function of the molecule is antisymmetrical with respect to the two X atoms (*i.e.*, the nuclear spin of the X atom is half integral). Then according to (63), we distinquish between two types of transitions in J as follows:

$$\left\{\begin{array}{llll} 0\rightarrow 1, & 2\rightarrow 3, & 4\rightarrow 5,\cdots & \text{in the } R \text{ branch}\\ & 2\rightarrow 2, & 4\rightarrow 4,\cdots & \text{in the } Q \text{ branch}\\ 2\rightarrow 1, & 4\rightarrow 3, & 6\rightarrow 5,\cdots & \text{in the } P \text{ branch}\end{array}\right. \tag{67a}$$

$$\left\{\begin{array}{llll} 1\rightarrow 2, & 3\rightarrow 4, & 5\rightarrow 6,\cdots & \text{in the } R \text{ branch}\\ 1\rightarrow 1, & 3\rightarrow 3, & 5\rightarrow 5,\cdots & \text{in the } Q \text{ branch}\\ & 3\rightarrow 2, & 5\rightarrow 4,\cdots & \text{in the } P \text{ branch}\end{array}\right. \tag{67b}$$

The transitions in (67a) involve levels whose spin wave functions are antisymmetrical, while those in (67b) involve levels whose spin wave functions are symmetrical. As the statistical weights of the levels involved in (67a) and (67b) are in the ratio $s:(s+1)$, it follows that the lines in (67a) and (67b) have a relative intensity ratio $s:(s+1)$, besides the factors given by (11), (12), (13) and (15). This causes an alternating intensity in the lines of the of the R, Q and P branches.

For the transition 0,0,0,→0,0,1. *i.e.*, the ν_3 fundamental, the vibrational wave function of the upper state is antisymmetrical, but that of the normal state is symmetrical as before. In this case, the symmetry characters of the rotational levels of the upper state are as shown in Fig. 23 (the total wave function is still assumed to be antisymmetrical with respect to the two X atoms as in Fig. 22)[5]. According to (63), we again distinguish between two types of transitions in J, namely,

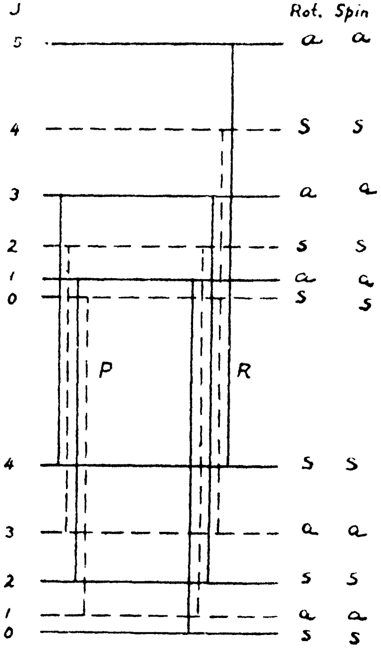

Fig. 23. Rotational structure of ν_3 band of linear YX_2

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[5] If the total wave function is symmetrical with respect to the two X atoms (*i.e.*, the nuclear spin of the X atom is whole integral multiple of $h/2\pi$), we have only to change the symmetry characters a and s under the heading "spin" in Figs. 22 and 23. The arguments remain unchanged.

$$\begin{cases} 0\rightarrow 1, \quad 2\rightarrow 3, \quad 4\rightarrow 5, \cdots\cdots & \text{in the } R \text{ branch} \\ 2\rightarrow 1, \quad 4\rightarrow 3, \quad 6\rightarrow 5, \cdots\cdots & \text{in the } P \text{ branch} \end{cases} \qquad (68a)$$

$$\begin{cases} 1\rightarrow 2, \quad 3\rightarrow 4, \quad 5\rightarrow 6, \cdots\cdots & \text{in the } R \text{ branch} \\ 1\rightarrow 0, \quad 3\rightarrow 2, \quad 5\rightarrow 4, \cdots\cdots & \text{in the } P \text{ branch} \end{cases} \qquad (68b)$$

Here there is no possibility for $\Delta J=0$ and the Q branch is missing. The R and P branch lines again show the alternating intensity ratio $s:(s+1)$ as before.

Let us finally consider the transition from the excited state 0,1,0→0,2,0 so that $l=1$ and $l'=2$. In this case, the vibrational wave functions are symmetrical for both the upper and the lower states. The symmetry characters of the rotational levels of the lower state are those shown for the upper state in Fig. 22, while those for the upper state are similar, except with J begining with 2. It is easy to see that in this case each line in the R, Q, and P branches

$$\begin{array}{llll} 1\rightarrow 2, & 2\rightarrow 3, & 3\rightarrow 4, \cdots\cdots & \text{in the } R \text{ branch} \\ & 2\rightarrow 2, & 3\rightarrow 3, \cdots\cdots & \text{in the } Q \text{ branch} \\ 2\rightarrow 1, & 3\rightarrow 2, & 4\rightarrow 3, \cdots\cdots & \text{in the } P \text{ branch} \end{array} \qquad (69)$$

arises from two transitions, one involving levels with antisymmetrical spin wave functions and the other symmetrical spin wave functions. Hence in such a band, no alternating intensities result as in the above fundamental bands.

In exactly the same way, the rotational lines of any harmonic or combination band can be examined.

The above results are not only applicable to the YX_2 molecules, but also to such molecules as actylene C_2H_2 or C_2D_2 and dicyanine C_2N_2, since the nuclear spin of the carbon atom is zero and we have only to consider the wave functions of the two H, D, or N atoms.

A very interesting case of the linear YX_2 molecule is when the nucleus of the X atom possesses no spin, *i.e.*, $s=0$. In this case, the levels involved in (67b) and (68b) are non-existent and the lines in (67b) and (68b) are missing. This is found to be the case in the carbon dioxide molecule.

The inclusion of the nuclear spins in the consideration of the symmetry properties of the rotational states of a molecule containing two or more identical atoms is important not only because it accounts for such phenonema as alternating intensities or missing lines in the vibration-rotational bands, but also because it furnishes a means for the determination of the spins of atomic nuclei. In fact, it is in this way that the spins of a number of atomic nuclei are obtained.

§4. Interactions between Vibrations and Rotations

The separate treatment in §2 of the vibration and the rotation of a molecule constitutes only what may be called an initial approximation to the actual problem, namely, the simultaneous vibration and rotation of a molecule. In this section we wish to show that certain features in the structure of the vibration-rotational bands of molecules which are not explained in the simple theory of §2 can be explained by taking into consideration the interactions between the vibrations and the rotations of the molecule.

A) Convergence in Vibration-rotational Lines

According to the simple theory of §2, the spacings of the rotational lines in the vibration-rotational bands of a linear molecule or a symmetrical top molecule are equidistant (see equations (47), (48), (51), (54) and (55)). It is found experimentally, however, that this is not the case; that there is usually a crowding together of the lines in the *R* branch and a spreading of the lines in the *P* branch, for high values of J. (see Fig. 24 below). This "convergence" of the lines can be shown to arise from the effect of the interactions between vibration and rotation of the molecule. To include this effect into the theory, it would be necessary to start with a Schroedinger equation in which the Hamiltonian is a function of all the coordinates of the atomic nuclei, which are subject only to the condition of conservation of linear momemtum (this amounts to the separation of the translational motion of the molecule as a whole from the Schrödinger equation). The exact solution of this equation is very difficult, if not impossible, for a molecule in general. Even in the case of a diatomic molecule, certain approximations must be made in obtaining a solution[1]. We shall in the following only give the treatment for the diatomic molecule as an illustration of the effect of the interactions. For more complicated molecules, the effect would be similar, although the analyses are much more complicated and further approximations are necessary in order to simplify the problem. In these cases, we shall be contented with the results that have been obtained rather than their detailed treatments.

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[1] J. L. Dunham, Phys. Rev. 41, 713, (1932), treats the problem of interaction between vibration and rotation by the W. K. B. method. See also J. E. Rosenthal and L. Motz, Phys. Rev. 51, 378, (1937).

Consider now a diatomic molecule of reduced mass μ, and let r be the internuclear distance (equilibrium separation r_0), ϑ and φ be the polar angles which the internuclear line makes with a fixed coordinate system. The Schrödinger equation can be shown to separate into the following three equations

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi, \tag{70}$$

$$\frac{d}{dx}\left[(1-x^2)\frac{d\Theta}{dx}\right] + \left[C - \frac{m^2}{1-x^2}\right]\Theta = 0, \quad x = \cos\vartheta, \tag{71}$$

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \left[\frac{8\pi^2\mu}{h^2}(E-V) - \frac{C}{r^2}\right]R = 0. \tag{72}$$

The separation constants m and C can be shown, in the same way as in (2) and (3), to be as follows: m=an integer, either positive or negative, and $C=J(J+1)$ where J is a positive integer. If the potential energy $V(r)$ of the molecule as a function of the nuclear separation be given by the Morse function (25) of Chap. III, equation (72) becomes

$$\frac{1}{y}\frac{d}{dy}\left(y\frac{d\psi}{dy}\right) + \frac{8\pi^2\mu}{a^2h^2}\left[\frac{E-D}{y^2} + \frac{2D}{y} - D - \frac{Ar_0^2}{y^2r^2}\right]\psi = 0, \tag{73}$$

in which

$$\psi = rR, \quad y = e^{-a(r-r_0)}, \quad A = \frac{h^2}{8\pi^2\mu r_0^2}J(J+1). \tag{74}$$

To solve this equation, let us expand $(r_0/r)^2$ as follows:[2]

$$\left(\frac{r_0}{r}\right)^2 = \left(1 - \frac{\log y}{ar_0}\right)^{-2}$$

$$= 1 + \frac{2}{ar_0}(y-1) + \left(-\frac{1}{ar_0} + \frac{3}{a^2r_0^2}\right)(y-1)^2 + \cdots. \tag{75}$$

On neglecting higher powers of (y−1) than the second, equation (73) becomes

$$\frac{1}{y}\frac{d}{dy}\left(y\frac{d\psi}{dy}\right) + \frac{8\pi^2\mu}{a^2h^2}\left[\frac{E-D-C_0}{y^2} + \frac{2D-C_1}{y} - (D+C_2)\right]\psi = 0 \tag{76}$$

where

$$C_0 = A\left(1 - \frac{3}{ar_0} + \frac{3}{a^2r_0^2}\right), \quad C_1 = A\left(\frac{4}{ar_0} - \frac{6}{a^2r_0^2}\right), \quad C_2 = A\left(-\frac{1}{ar_0} + \frac{3}{a^2r_0^2}\right).$$

On making the substitutions similar to (27) and (28) of Chap. III,

$$\psi = e^{-\frac{z}{2}} z^{\frac{\beta}{2}} F(z),$$

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[2] C. L. Pekeris, Phys. Rev. 45, 98, (1934).

$$z = 2ay, \qquad \alpha = \frac{2\pi\sqrt{2\mu(D+C_0)}}{ah}, \qquad E - D - C_0 = -\frac{a^2h^2\beta^2}{32\pi^2\mu}, \tag{77}$$

and proceeding in exactly the same way as in (29)-(33) of Chap. III, one obtains to a first approximation the eigenvalues

$$\begin{aligned} E/h &= \nu(v + \tfrac{1}{2}) - x\nu(v + \tfrac{1}{2})^2 + B_0 J(J+1) \\ &\quad - \alpha_e(v + \tfrac{1}{2}) J(J+1) - \xi J^2(J+1)^2 \end{aligned} \tag{78}$$

in which ν and x are given by (32) and (33) of Chap. III, and

$$B_0 = \frac{h}{8\pi^2 I_0 c}, \qquad \alpha_e = 6B_0 x\left(\sqrt{\frac{B_0}{x\nu}} - \frac{B_0}{x\nu}\right), \qquad \xi = \frac{4}{\nu^2}B_0^3. \tag{79}$$

For convenience, all the quantities ν, $x\nu$ B_0, α_e and ξ in (78) and (79) are expressed in wave numbers (cm^{-1}), *i.e.*, the frequency divided by the velocity of light c. The first two terms in (78) are the energy of the non-rotating oscillator, the third term is the energy of the non-vibrating rotator, the fourth term represents the energy due to the interactions between vibration and rotation,[3] and the last term represents the effect of the centrifugal action on the rotational energy.

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[3] In the above derivation of the term $-\alpha_e(v+\frac{1}{2})(J+1)J$, it is perhaps not very clear just how the interactions between vibration rotation produce this energy change. We shall see that this energy change comes about from two causes: First, because of the vibration, the moment of inertia I of the molecule is not a constant, but varies periodically. To find the change in the energy of rotation due to this change in the moment of inertia, we may in a first approximation regard the vibration as simple harmonic. A detailed analysis shows that the energy change is given by the second term in α_e in (79), which is independent of x, namely, $\frac{6B_0^2}{\nu}(v+\frac{1}{2})J(J+1)$. This term is positive since the effective moment of inertia during the vibration can be shown to be less than the equilibrium value I_0 and since the energy of rotation depends of I through $1/I$. Secondly, the centrifugal force developed by the rotation stretches the separation between the atoms by an amount depending on both the force constant between them and the state of rotation. If the vibration is strictly simple harmonic, this displacement of the equilibrium separation will not change the frequency of vibration in a first approximation. If the vibration is anharmonic, an analysis shows that the frequency and hence the energy of vibration are changed by amounts depending on both the anharmonic potential and the state of rotation. In the case of the anharmonic oscillator with the Morse potential, this energy change is given by the first term of α_e in (79), namely, $-6B_0x\sqrt{\frac{B_0}{x\nu}}(v+\frac{1}{2})J(J+1)$. This term is negative. As $B_0 < x\nu$ for all molecules whose spectra are known, it follows that the total energy change in (78) is negative.

This situation is more clearly brought out by the treatments of the linear YX_2 molecule by Adel and Dennison, Phys. Rev. 44, 99, (1933), and of C_2H_2 by T. Y. Wu, to appear in Jour. Chem. Phys. (1940).

Before considering the change in the structure of the vibration-rotational band brought about by the terms in α_e and ξ, it is well to have some idea as to the order of magnitude of the various terms in the energy expression (78) for a few common molecules. For the hydrogen halides, the observed values of ν, $x\nu$, B_o, α and ξ are as follows:[4]

	ν cm^{-1}	$x\nu$ cm^{-1}	B_o cm^{-1}	$I_o \times 16^{40}$	α_e cm^{-1}	ξ cm^{-1}
HF	4141	90.8	20.924	1.322	0.763	0.00215
HCl	2989	51.65	10.591	2.612	0.302	0.00052
HBr	2649.7	(44)	8.476	3.263	0.230	0.00034

Table III

It is seen that the effect of the last term in (78) is small in these molecules. It is found that in other molecules not containing hydrogen, the values of B_o and α_e are usually smaller than those given above and the term in ξ can be entirely neglected except for very high values of J.

Consider now the vibration-rotational band corresponding to the transition in v from 0 to 1. The frequencies of the rotational lines in the R and P branches are given by

$$R \text{ branch } J \rightarrow J+1: \quad \nu = \nu_0 - 2x\nu_0 + 2B_0(J+1) - \alpha_e(J+1)(J+3) - 4\xi(J+1)^3,$$

$$P \text{ branch } J+1 \rightarrow J: \quad \nu = \nu_o - 2x\nu_0 - 2B_0(J+1) - \alpha_e(J-1)(J+1) + 4\xi(J+1)^3,$$

or

$$\nu = \nu_0 (1 - 2x) + 2 (B_o - \alpha_e)\, m - \alpha_e m^2 - 4\, \xi\, m^3 \qquad (80)$$

where $m = \pm 1, \pm 2, \pm 3, \ldots\ldots$ It is seen that the term $-\alpha_e m^2$ gives rise to a "convergence" of the rotational lines, that is, a crowding of the lines in the R branch and a spreading of the lines in the P branch, as the ordinal number m of the lines increases. The effect of the term $4\,\xi\, m^3$ is to accentuate the crowding of the lines in the R branch but to offset the spreading in the P branch. As $4\,\xi \ll \alpha_e$, the effect of the $\alpha_e m^2$ term always predominates. Typical examples of this convergence are found in the infrared absorption bands of the hydrogen halides. The following figure is taken from the work of Meyer and Levin.[5]

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[4] H. Sponer, *Molekülspektren*, I, P. 26, (1936).

[5] C. F. Meyer and A. A. Levin, Phys. Rev. 34, 44, (1929); analysis of data by W. F. Colby, Phys. Rev. 34, 53, (1929).

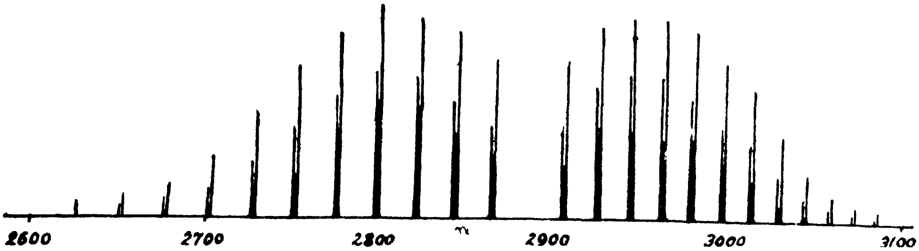

Fig. 24. The fundamental band of HCl. The doubling of each line is due to the presence of the two isotopes 35 and 37 of chlorine.

The general theory of the energy of a vibrating rotating molecule has been studied by Eckart, Van Vleck, Wilson and Howard,[6] and has been applied to the case of a linear triatomic molecule by Weinberg and Eckart,[7] and a linear tetratomic molecule by Sayvetz[8] and Wu.[9] It is beyond the scope of this volume to give the general theory; but the idea and the results can be sufficiently made clear by taking the symmetrical linear YX_2 molecule as an example. For the general and other particular cases, reference must be made to the above mentioned papers.

Let a moving coordinate system be chosen as shown in Fig. 21. Let the coordinates of the ith atom in this moving system be ξ_i, η_i, ζ_i and let the normal coordinates of the vibrations ν_1, ν_2, ν_3 be q_1, q_2, q_3, (Fig. 3). Then from the choice of the moving system and the nature of the normal vibrations, one has

$$\xi_i = 0, \qquad \eta_i = b_i q_2, \qquad \zeta_i = c_i + c_{i1} q_1 + c_{i3} q_3 \tag{81}$$

where c_i is the equilibrium distance of the *i*th atom from the origin. The condition that the origin of the moving system always lie at the centre of mass

$$\Sigma m_i \xi_i = \Sigma m_i \eta_i = \Sigma m_i \zeta_i = 0$$

and the condition that the angular momentum be zero as the equilibrium configuration is approached

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[6] C. Eckart; J. H. Van Vleck; see references on P. 112; E. B. Wilson, Jr. and J. B. Howard, Jour. Chem. Phys. 4, 260, (1936).

[7] A. Weinberg and C. Eckart. *ibid.* 5, 517, (1937); also A. Adel and D. M. Dennison, Phys. Rev. 44, 99, (1933).

[8] A. Sayvetz, Jour. Chem. Phys. 7, 383, (1939).

[9] T. Y. Wu, to appear in Jour. Chem. Phys. (1940).

$$\lim_{q\to 0} \Sigma\, m_i (\eta_i \dot{\zeta}_i - \zeta_i \dot{\eta}_i) = 0$$

lead to

$$\begin{aligned} \Sigma\, m_i c_i = \Sigma\, m_i b_i = \Sigma\, m_i c_{i1} = \Sigma m_i c_{i3} = 0 \\ \Sigma\, m_i b_i c_i = \Sigma\, m_i b_i c_{i1} = \Sigma\, m_i b_i c_{i3} = 0. \end{aligned} \tag{82}$$

These relations completely determine the coefficients b_i and $c_{i\lambda}$ except for a multiplicative constant. Following Weinberg and Eckart, we shall let

$$\begin{gathered} b_1 = b_3 = \frac{1}{m}\, a \left[\frac{m^2 M}{M+2m}\right]^{\frac{1}{2}}, \qquad b_2 = \frac{2a}{M} \left[\frac{m^2 M}{M+2m}\right]^{\frac{1}{2}}, \\ c_{11} = -c_{31} = a, \qquad c_{13} = c_{33} = b_1, \qquad c_{23} = 0\,, \qquad c_{21} = 0 \end{gathered} \tag{83}$$

where a is the equilibrium distance between the Y and the X atoms. The normal coordinates become then dimensionless (which are related to the coordinates employed in (81) on P. 66 through $q_1 = \left(\frac{h}{4\pi^2 I\omega_1}\right)^{\frac{1}{2}} \sigma$, etc.), and further we have

$$\Sigma\, m_i b_i^2 = \Sigma\, m_i c_i^2 = \Sigma\, m_i c_{i\lambda}^2 = 2m\, a^2 = I \tag{84}$$

where I is the equilibrium value of the moment of inertia.

The kinetic energy of the molecule due to the normal vibrations is

$$\begin{aligned} 2\,T &= \Sigma\, m_i (\dot{\xi}_i^2 + \dot{\eta}_i^2 + \dot{\zeta}_i^2) + \Lambda_\xi\, \Omega_\xi \\ &= I\,(\dot{q}_1^2 + \dot{q}_2^2 + \dot{q}_3^2) + \Lambda_\xi\, \Omega_\xi \end{aligned} \tag{85}$$

where Ω_ξ is the ξ-component of the angular velocity due to the rotation of the molecule, and Λ_ξ is the only non-vanishing component of the angular momentum due to the normal vibrations

$$\begin{aligned} \Lambda_\xi &= \Sigma\, m_i (\eta_i \dot{\zeta}_i - \dot{\eta}_i \zeta_i) = I\,(q_2 \dot{q}_3 - \dot{q}_2 q_3), \\ \Lambda_\eta &= \Lambda_\zeta = 0. \end{aligned} \tag{86}$$

The momenta conjugate to the q's are, from (85),

$$p_1 = I\,\dot{q}_1, \qquad p_2 = I\,\dot{q}_2 - I\, q_3 \Omega_\xi, \qquad p_3 = I\,\dot{q}_3 + I\, q_3 \Omega_\xi\,. \tag{87}$$

The total angular momentum due to both the rotation and the vibration of the molecule is given by[10]

$$\begin{aligned} M_\xi &= A_{\xi\xi}\,\Omega_\xi + \Lambda_\xi \\ M_\eta &= A_{\eta\eta}\,\Omega_\eta - A_{\eta\zeta}\,\Omega_\zeta \\ M_\zeta &= -\,A_{\eta\zeta}\,\Omega_\eta + A_{\zeta\zeta}\,\Omega_\zeta \end{aligned} \tag{88}$$

where the $A_{\xi\xi}, A_{\eta\zeta} \ldots$ are the moments and products of inertia of the molecule along the moving axes and can be shown to be

$$\begin{aligned} &A_{\xi\xi} = I\,(g^2 + q_2^2 + q_3^2), \quad &&A_{\eta\eta} = I\,(g^2 + q_3^2), \quad &&A_{\zeta\zeta} = I\,q_2^2, \\ &A_{\eta\zeta} = I\,q_2\,q_3, &&A_{\xi\eta} = A_{\xi\zeta} = 0, &&g = 1 + q_1. \end{aligned} \tag{89}$$

The kinetic energy of the vibrating rotating molecule is[10]

$$2\,T = \Sigma\, p_i\,\dot{q}_i + M_\xi\,\Omega_\xi + M_\eta\,\Omega_\eta + M_\zeta\,\Omega_\zeta$$

or

$$2\,I\,T = p_1^2 + p_2^2 + p_3^2 + \frac{M_\zeta^2}{q_2^2} + \frac{[M_\xi - \Lambda]^2}{g^2} + \frac{[M_\eta + \frac{q_3}{q_2} M_\zeta]^2}{g^2} \tag{90}$$

where

$$\Lambda = q_2\,p_3 - p_2\,q_3 \tag{91}$$

The Hamiltonian is $T+V$, where V is, up to the second order, the sum of the expressions in (81a), (83) and (84) on P. 67. The first four terms in (90) correspond to the expression for T in (81a) on P. 67. On treating the last two terms as perturbations—a process which is justified since the energy of rotation and that of the interaction between vibration and rotation are essentially smaller than that of vibrations —, one obtains the zeroth-order energy and eigen functions as given by (82) on P. 67. The contributions to the energy from the last two terms in (90) can be obtained as follows: In a first approximation, we shall replace $g=1+q_1$ by 1 and the diagonal elements are

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[10] See, for example, A. G. Webster, Dynamics of Particles and of Rigid, Elastic and Fluid Bodies, P. 249.

$$\begin{aligned}
(M_\zeta^2)^{R}_{R} &= l^2 (h/2\pi)^2 \\
(M_\xi^2 + M_\eta^2)^{R}_{R} &= [J(J+1) - l^2] (h/2\pi)^2 \\
(\Lambda^2)^{V}_{V} &= \left[(v_2 + 1)(v_3 + \tfrac{1}{2})\left(\frac{\omega_3}{\omega_2} + \frac{\omega_2}{\omega_3}\right) - 1 \right] (h/2\pi)^2 \\
&\quad - (v_3 + \tfrac{1}{2}) \frac{\omega_2}{\omega_3} (h/2\pi)^2 l^2 \int \frac{1}{q_2^2} \psi_{v_2}^2 q_2 \, dq_2 \\
\left(\frac{q_3^2}{q_2^2} M_\zeta^2\right)^{VR}_{VR} &= (v_3 + \tfrac{1}{2}) \frac{\omega_2}{\omega_3} (h/2\pi)^2 l^2 \int \frac{1}{q_2^2} \psi_{v_2}^2 q_2 \, dq_2,
\end{aligned} \tag{92}$$

use being made of the following relation which is obtainable from (43) on P. 53

$$\int_0^\infty \varrho \left[\left(\frac{d\psi_{v_2}}{d\varrho} \right)^2 + \frac{l^2}{\varrho^2} \psi_{v_2}^2 \right] d\varrho = v_2 + 1.$$

The first order energy is hence

$$\frac{h^2}{8\pi^2 I} [J(J+1) - l^2] + \frac{h^2}{8\pi^2 I} \left[(v_2 + 1)(v_3 + \tfrac{1}{2}) \left(\frac{\omega_3}{\omega_2} + \frac{\omega_2}{\omega_3} \right) - 1 \right] \tag{93}$$

The first term is simply the energy of rotation while the second term gives the energy of interaction between the parallel vibration $\mathbf{v}_3$ and the perpendicular vibration $\mathbf{v}_2$ as the result of the extra angular momentum arising from these vibrations. This second term is independent of the rotational quantum numbers and hence does not affect the rotational structure of the bands. Its presence can be taken care of in (87) of P. 68 by replacing the constant i by

$$i + \frac{h}{8\pi^2 I} \left(\frac{\omega_3}{\omega_2} + \frac{\omega_2}{\omega_3} \right). \tag{94}$$

The interaction between the vibration and the rotation appears in the next approximation. First the factor $1/g^2$ in the last two terms in (90) represents the variation of the moment of inertia of the molecule with the vibrational motion. This changes the energy of the molecule in two ways. The quadratic part of $1/g^2 = 1 - 2q_1 + 3q_1^2$ introduces a factor

$$1 + \frac{3h}{4\pi^2 I \omega_1} (v_1 + \tfrac{1}{2})$$

for the energy expression in (93). The linear term in $1/g^2$ causes the appearance of a term linear in the normal coordinate q_1 and entails a transformation to a new normal coordinate $\overset{*}{q}_1$ to take into account the change of the equilibrium distance a brought about by this additional energy term. This transformation introduces, when applied to the first order perturbation potential (83) on P. 67, terms that are quadratic in the normal coordinates and contain the constants in the first order potential. The diagonal elements of these terms are of the order[9]

$$\frac{h^2}{8\pi^2 I}\,[J\,(J+1)-l^2]\,\frac{h}{4\pi^2 I\,\omega}\,k\,(v+\tfrac{1}{2}) \tag{95}$$

where k is a constant in the first order (cubic) potential.

Secondly, the term $M_\xi\Lambda$ in (90) gives a second order perturbation according to (16) on P. 48. The evaluation of the non-vanishing non-diagonal elements of $M_\xi\Lambda$ can be performed with the known vibrational wave functions and the rotational wave functions (of a symmetrical rotator). The order of magnitude is again that of (95), but this contribution is characterized by the appearance of the denominators $\omega_3+\omega_2$ and $\omega_3-\omega_2$. Hence it may be expected to have important effect on the band structure when ω_2 and ω_3 are close to each other.[11]

On combining these various second order contributions, it can be shown that the total energy of a vibrating rotating molecule is of the form

$$E/h=(E_{vib}+E_{rot})/h+B_0\,[J\,(J+1)-l^2]\,[\Sigma\,(v_i+\mu_i)\,\alpha_i] \tag{96}$$

where μ_i is $\frac{1}{2}$ for the parallel and 1 for the perpendicular vibrations, and the α's are constants depending on the fundamental frequencies, the moment of inertia and the first order anharmonic constants. The rotational lines of a band arising from transitions from the normal vibrational state to a state v_1, v_2, v_3 are given by an expression of the form

$$\nu=\nu_{vib}+B_0\,[2+\sum_i(v_i+2\mu_i)\,\alpha_i]\,N+B_0\,[\Sigma\,v_i\,\alpha_i]\,N^2 \tag{97}$$

where N is the ordinal number, 0, ±1, ±2...of the lines. The quadratic term causes a convergence of the rotational lines similar to that in (80) for a diatomic molecule. From the convergence and the empirical values of the constant $B_v = B_0[1+\Sigma(v_i+2\mu_i)\alpha_i]$ for a few vibrational states, it is possible to determine the α's. The theoretical expressions for the α's then furnish three further relations for the determination of the first order anharmonic constants.

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[11] The importance of these second order terms with the resonance denominators is first emphasized by Professor D. M. Dennison in private communications. His results on the CO_2 molecule will probably be published shortly.

In other molecules, the effect of the interaction between vibration and rotation can probably be still represented by an expression of the form (96), although it would no longer be easy to obtain the theoretical expressions for the α's.

B). Coriolis Perturbation

Another effect arising from the interaction between the vibration and the rotation besides the convergence of the rotational lines discussed in the last section is the anomaly in the spacings of the Q branches of the component bands in the perpendicular type bands of axially symmetrical molecules. From the simple theory of the symmetrical rotator given in §2, B), it follows that the separation between these Q branches is given by $\frac{h}{4\pi^2 I_A} \cdot \beta$ where $\beta = \frac{I_A}{I_C} - 1$, and that this separation should be the same for all the perpendicular bands of the same molecule. It was found, however, that in the case of the methane CH_4[1] and the methyl halides[2] spectra, the separations between the Q branches are not constant but are different in different perpendicular bands of the same molecule. This is not understandable from the simple theory of the symmetrical rotator. It was first suggested by Teller[3] that the explanation of this anomaly lies in the interaction between the vibration and the rotation of the molecule in the following manner: As the result of the slow (compared with the vibration) rotation of the molecule about the symmetry axis, a Coriolis force is developed in the perpendicular vibrations (which are doubly degenerate because of the isotropy in directions perpendicular to the symmetry axis), and this gives rise to an "internal" angular momentum which changes the energy of the molecule and hence the separation of the Q branches. The theory has been worked out further in details for the axially symmetrical molecules such as YX_3, ZYX_3 and YX_4 by Johnston and Dennison.[4] From a close study of the vibrational and the rotational motions of these molecules, it was found that while the internal angular momentum due to the vibration is different for different bands and depends in a rather complicated manner on the masses of the atoms and the constants in the potential energy of the molecule, there are certain "sum rules" that are independent of the potential function. We must refer to the works of Teller and of Johnston and Dennison for the details of the theory; but the results, which are very useful for our discussion of such molecules in Chap. V, can be conveniently summarized as follows.

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[1] J. P. Cooley, Astrophys. Jour. 62, 73, (1925).

[2] W. H. Bennett and C. F. Meyer, Phys. Rev. 32, 888, (1928).

[3] E. Teller, *Hand-und Jahrbuch d. Chem. Physik* 9/II, (1934).

[4] M. Johnston and D. M. Dennison, Phys. Rev. 47, 94; 48, 868, (1935).

Let the internal angular momentum due to the perpendicular vibration ν_i be $\xi_i\,(h/2\pi)$, and let the spacing of the Q branches in the band ν_i be denoted by $\Delta\nu_i$. Then for YX_3, ZYX_3 and YX_4 respectively,

$$\Delta\nu_i = \left[\frac{1-\xi_i}{I_C} - \frac{1}{I_A}\right]\frac{h}{4\pi^2}, \qquad \Delta\nu_i = \frac{1-\xi_i}{I}\cdot\frac{h}{4\pi^2}. \tag{98}$$

	YX_3	ZYX_3	YX_4
$\Sigma\,\xi_i$	$\frac{I_C}{2\,I_A} - 1$	$\frac{I_C}{2I_A}$	$\frac{1}{2}$
$\Sigma\,\Delta\nu_i$	$\left(\frac{3}{I_C} - \frac{5}{2I_A}\right)\frac{h}{4\pi^2}$	$\left(\frac{3}{I_C} - \frac{7}{2I_A}\right)\frac{h}{4\pi^2}$	$\frac{3}{2I}\cdot\frac{h}{4\pi^2}$
$\xi\,(2\nu_i)$	$-\,2\,\xi_i$	$-\,2\,\xi_i$	$-\,\xi_i$
$\xi\,(3\nu_i)$	ξ_i	ξ_i	
$\xi(\nu_i+\nu_j)$	$-\,(\xi_i + \xi_j)$	$-\,(\xi_i + \xi_j)$	$-\,\frac{1}{4}$

Table IV. Internal angular momenta in axially symmetrical molecules[5]

In a band $\nu_i + \nu_{\parallel}$ where $\nu_{\parallel}$ is a parallel type vibration, the internal angular momentum and hence the separation $\Delta\nu$ are the same as in the band ν_i since the parallel vibration contributes nothing to the internal angular momentum.

This theory of Coriolis interaction is important not only because it furnishes an explanation of the anomalous spacings in the perpendicular type bands of axially symmetrical molecules, but also because (i) the relations (98) and Table IV make it possible to obtain the moments of inertia of the molecule from the observed spacings $\Delta\nu$, and

---

[5] In Table IV, the perpendicular vibrations of YX_3 are ν_2 and ν_4; those of ZYX_3 are ν_2, ν_4, ν_6; and those of YX_4 are ν_3 and ν_4. For the modes of these vibrations, see Figs. 26, 32, and 31 respectively.

(ii) in the case of the tetrahedral YX_4 molecule, a knowledge of the spacings $\Delta\nu_3$ and $\Delta\nu_4$ makes it possible to determine one of the five constants in the most general potential function of the molecule.

Nielsen has applied the same idea to the "perpendicular" vibrations ν_5 and ν_6 of the formaldehyde molecule. Recently a detailed study of the Coriolis perturbations in the YX_4 molecule has been made by Jahn, and the result has been applied to the CH_4 molecule by Jahn and Childs with success. We shall discuss the spectra of all such molecules as YX_3, ZYX_3, YX_4, and ZYX_2 in the following chapter.

CHAPTER V

VIBRATOINAL SPECTRA OF MOLECULES: EMPIRICAL RESULTS

In this chapter, we shall summarize the results of infrared and the Raman effect studies of polyatomic molecules. The data are examined with special regard to the symmetry properties of the molecules and their normal vibrations, the interpretations of the observed frequencies, and the potential functions of the molecules. The theoretical basis of these discussions has been presented in Chapters II, III and IV and we need perhaps only a few remarks here concerning the notations employed.

(i) For the normal vibrations in certain molecules possessing certain elements of symmetry, the notations employed by Mecke and others, namely, those distinguishing between the "valence" vibrations and the "deformation" vibrations δ, with subscripts s and a for vibrations symmetrical and antisymmetrical with respect to an element of symmetry, and the subscripts π and σ for vibrations which are parallel and perpendicular to an axis of symmetry, are most descriptive. On the other hand, for molecules possessing a large number of normal vibrations, these notations become impractical and the conventional numerical notations employed by Dennison are convenient. In still other cases, it may be desirable to describe the vibrations by the symmetry class to which they belong, followed by a descriptive notation giving the approximate nature of the vibration. Perhaps the choice of these notations will remain to be determined by convenience, usage and individual taste. In the following, these different notations are employed in different molecules, the choice being determined by these factors.

(ii) Although it is the wave lengths that are directly measured rather than the frequencies, we shall in the following give only the frequencies in wave numbers (cm^{-1}), since these are more convenient for considerations of the energy states of the molecule. This will do away with the unnecessary effort of translating the wave lengths in μ into wave numbers by one who is thinking in terms of energy states. To him, the reading of the more experimental papers on infrared spectra, in which the bands are mentioned by their wave lengths in μ, causes no little inconvenience.

(iii) In all the equations giving the normal frequencies, if the frequencies $\tilde{\nu}$ be expressed in units of 1000 cm^{-1} and $\lambda=\tilde{\nu}^2$, the atomic masses in units of the mass of the hydrogen atom (or more accurately, simply the atomic weights), the potential constants so obtained are in units of 0.5875×10^5 dynes/cm. Unless otherwise mentioned, the values of the potential constants given are in 10^5 dynes/cm.

§1. Triatomic Molecules

A) Linear Molecules

1) CO_2

This molecule is of special interest not only because of its common occurrence, but because it shows the kind of accidental degeneracy discussed in Chap. III, §4, B. It is one of the few molecules whose spectra and structure are known in considerable detail.

That the molecule is linear and symmetrical is definitely established on the following evidences: (1) the permanent electric moment is zero,[1] (2) the rotational structure of the vibration-rotational bands is consistent with a linear and symmetrical model,[2] and (3) the whole system of vibrational bands satisfies the selection rules for the linear symmetrical model given in (92a) and (92b) in Chap. III,[2] not to mention the many other chemical evidences. Such a molecule possesses an infrared inactive, Raman effect active vibration ν_1, a perpendicular (degenerate) infrared active vibration ν_2, and a parallel infrared active vibration ν_3. The frequency ν_1 should appear in the Raman spectrum as a single line (accompanied of course by wings due to the rotational lines). It was found, however, that two lines appear at 1285.8 and

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[1] See, for example, H. A. Stuart, Zeits. f. Physik 47, 457; 51, 490, (1928). Also *Landolt-Bornstein Tables.*

[2] P. E. Martin and E. F. Barker, Phys. Rev. 41, 291, (1932), analyzed the rotational structure of the ν_2 band at 667 cm^{-1}. That the lines are regularly spaced shows that the molecule must be linear; that the band possesses a Q branch shows that it arises from a vibration in which the change of the electric moment is perpendicular to the axis of the molecule; that every other line is missing in both the P and the R branches shows that (i) the molecule must have a symmetry center, and (ii) the spin of the oxygen nucleus must be zero, according to §3, Chap. IV.

1388.4 cm^{-1} with an intensity ratio of about 0.61.[3] This is explained by Fermi as due to a resonance between ν_1 and $2\nu_2$, resulting in a mutual sharing of the wave functions of the two states and hence in the appearance of two lines instead of one.[4] The theory has then been further developed and applied to the infrared spectrum by Dennison[5] and by Adel and Dennison,[6] who carried out a second order perturbation calculation of the anharmonicity as well as a first order calculation for the resonance interaction, as shown in Chap. III, §3, A and §4, B. We give in the following table the observed bands, their classifications and the frequencies culculated according to the theory of Dennison and Adel.

The observers of the various bands are given in footnote (7). The bands marked by an asterisk are those employed in the evaluation of the anharmonicity coefficients, by means of (132), Chap. III. The result is

$$\begin{array}{llll} |b| = 72.9 & \nu_1 = 1321.7 & x_{11} = -1 & x_{12} = -2.3 \\ \Delta = 14.7 & \nu_2 = 667.9 & x_{22} = 0.74 & x_{23} = -10.9 \\ x_{ll} = -0.74 & \nu_3 \doteq 2362.8 & x_{33} = -12.7 & x_{13} = -22.1 \end{array} \tag{1}$$

From these coefficients, it is possible to calculate the zeroth order frequencies from (75), Chap. III,

$$\omega_1 = 2\omega_2 + \Delta = 1361, \qquad \omega_2 = 673, \qquad \omega_3 = 2397. \tag{2}$$

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[3] Early work on the Raman spectrum of the CO_2 gas was done by R. G. Dickinson, R. T. Dillon, and F. Rasetti, Phys. Rev. 34, 582, (1929). Later measurements were made by Isabel Hanson, Phys. Rev. 46, 122, (1934), and A. Langseth and J. Rud Nielsen, Phys. Rev. 46, 1057, (1934). Attempt to explain one of the two strong lines, namely, 1388.4 cm^{-1}, as the overtone of the fundamental $\nu_2 = 667$ fails for two reasons: (i) an overtone can hardly have the observed great intensity, and (ii) the overtone of the degenerate vibration ν_2, if observed, would be expected to be completely depolarized, while the observed degrees of depolarization of both lines 1285.8 and 1388.4 cm^{-1} are very low (~ 0.18 and ~ 0.14 respectively), according to the measurement of Langseth and Nielsen, loc. cit.

[4] E. Fermi, Zeits. f. Physik 71, 250, (1931).

[5] D. M. Dennison, Phys. Rev. 41, 304, (1932).

[6] A. Adel and D. M. Dennison, Phys. Rev. 43, 716, (1933).

[7] M. B.=Martin and Barker, Phys. Rev. 41, 291, (1932); B.=Barker, Astrophys. Jour. 55, 321, (1922); D. D. R.=Dickenson, Dillon and Rasetti, Phys. Rev. 34, 582, (1929); B. W.=Barker and Wu, Phys. Rev. 45, 1, (1934); H. V.=Herzberg and Verleger, Phys. Rev. 48, 706, (1935); the bands are observed with the photographic technique. The band centers given here are estimated from the band heads only; A. D.=Adams and Dunham, Pub. A. S. P. 44, 243, (1932), measured these bands in the absorption spectrum of the atmosphere of the planet Venus; B. A.=Barker and Adel, Phys. Rev. 44, 185, (1933).

Transitions $v_1\,v_2\,l\,v_3 \rightarrow$	$v_1\,v_2\,l\,v_3$	cm^{-1} obs.	Band type obs.	cm^{-1} calc.	Observers[7]
0 0 0 0	0 1 1 0	667.5 **	⊥	667.9	M. B.
	1 0 0 0	1285.8 *	Raman	1286.3	D. D. R.
	0 2 0 0	1388.4 *	Raman	1387.9	D. D. R.
	0 2 2 0	(1336.2) *		1335.8	
	1 1 1 0	1933.5 *	⊥	1933.2	M. B.
	0 3 1 0	2077.1 *	⊥	2077.4	M. B.
	0 0 0 1	2350.1 *	‖	2350.1	M. B.
	1 0 0 1	3610	‖	3614	B.
	0 2 0 1	3717	‖	3716	B.
	2 0 0 1	4860	‖	4852	B. W.
	1 2 0 1	4982 *	‖	4982	B. W.
	0 4 0 1	5110	‖	5109	B. W.
	3 0 0 1	6079	‖	6078	B. W.
	2 2 0 1	6233	‖	6233	B. W.
	1 4 0 1	6353	‖	6352	B. W.
	0 6 0 1	6512	‖	6512	B. W.
	0 0 0 3	6978	‖	6974	B. W.
	1 0 0 3	8193	‖	8188	H. V.
	0 2 0 3	8293	‖	8291	H. V.
	0 0 0 5	11496.5 *	‖	11496.5	A. D.
	1 0 0 5	12672.4 *	‖	12672.4	A. D.
	0 2 0 5	12774.7 *	‖	12774.7	A. D.
0 1 1 0	1 0 0 0	720.9	⊥		M. B.
0 1 1 0	0 2 0 0	618.3	⊥		M. B.
0 1 1 0	0 2 2 0	668.5	⊥		M. B.
0 1 1 0	1 1 1 0	1408.4	Raman		
0 1 1 0	0 3 1 0	1264.5	Raman		
0 1 1 0	2 0 0 0	1886	⊥		B. W.
0 1 1 0	1 2 0 0				
0 1 1 0	0 4 0 0	2137	⊥		B. W.
0 1 1 0	1 2 2 0	2049	⊥		B. W.
0 1 1 0	1 1 1 0	1264.5	Raman	1265.3	D. D. R.
0 1 1 0	0 3 1 0	1408.4	Raman	1409.5	D. D. R.
1 2 0 0	1 1 1 0	791.0	⊥		M. B.
0 2 0 0	0 3 1 0	647.8	⊥		M. B.
0 2 2 0	1 1 1 0	741.0	⊥		M. B.
0 2 2 0	0 3 1 0	597.0	⊥		M. B.
1 0 0 0	0 0 0 1	961.0	‖	962.2	B. A.
0 2 0 0	0 0 0 1	1063.8	‖	1063.7	B. A.

Table V. Vibrational spectrum of CO_2

The zeroth order (quadratic) potential constants in a potential of the form

$$2V = k\Big[(\delta r_1)^2 + (\delta r_2)^2\Big] + 2k_1\,\delta r_1\,\delta r_2 + k_\alpha\,(r\delta\alpha)^2 \tag{3}$$

can be calculated from the equations

$$\begin{aligned} \lambda_1 + \lambda_3 &= \frac{2(M+m)}{mM}\,k - \frac{2}{M}\,k_1, \\ \lambda_1\lambda_3 &= \frac{M+2m}{m^2M}\,(k^2 - k_1^2), \\ \lambda_2 &= \frac{2(M+2m)}{mM}k_\alpha\,. \end{aligned} \tag{4}$$

The result is

$$k = 15.9, \qquad k_1 = 1.06, \qquad k_\alpha = 0.58 \text{ in } 10^5 \text{ dy/cm}, \tag{5}$$

From the rotational line spacings in the ν_2 fundamental, Martin and Barker obtained the value 70.8×10^{-40} g.cm^2 for the moment of inertia of the molecule. This gives the value 1.15Å for the carbon-oxygen distance.[9] Hence

$$k_\alpha\, r^2 = 0.78\times10^{-11} \text{ dynes cm/radian.} \tag{5a}$$

The constants in the first and the second order potentials (83) and (84) of Chap. III can be calculated from equs. (87) and (131). The values of the constants a and c have been accurately determined by Adel and Dennison from the convergence factors in the ν_3 band measured by Martin and Barker, and the $5\nu_3$, $5\nu_3+\nu_1$, $5\nu_3+2\nu_2$ bands

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[8] Because of the resonance between ν_1 and $2\nu_2$, the two bands 1286.3, 1387.9 cm^{-1} are to be ascribed to transitions from the normal state to states whose wave functions are given by ψ_- and ψ_+ in (133) of Chap. III, respectively. Hence in obtaining (87) and (88) from (86) of Chap. III, it is necessary to multiply the integrals in σ and ϱ by the appropriate factors α^2 and β^2 given by (134). Thus from Table II, one obtains

$$\tfrac{1}{2}\Delta - \frac{|b|}{\sqrt{2}}(1+\tfrac{1}{2}y^2) + \beta^2(\nu_1 + x_{11}) + \alpha^2(2\nu_2 + 4x_{22}) = 1286.3,$$

$$\tfrac{1}{2}\Delta + \frac{|b|}{\sqrt{2}}(1+\tfrac{1}{2}y^2) + \alpha^2(\nu_1 + x_{11}) + \beta^2(2\nu_2 + 4x_{22}) = 1387.9.$$

Similar arguments hold for the other resonating levels, such as $n\nu_1$, $(n-1)\nu_1+2\nu_2$, $(n-2)\nu_1+4\nu_2$, etc.

[9] Electron diffraction measurements of Wierl, Ann. der Physik 13, 453, (1932), give 1.18±.04A for the C—O distance. Cf, Brockway, Rev. Mod. Phys. 8, 231, (1936).

photographed by Adams and Dunham from the absorption spectrum of the atmosphere of Venus. The result is as follows:[10]

$$\begin{array}{lll} a = -\ 36.2, & d = 1.8 & g = -\ 7.9, \\ b = \ 72.9, & e = 2, & j = \ 3.3, \\ c = -\ 202.1, & f = 1.1, & i = -\ 23.2. \end{array} \qquad (6)$$

These values define the potential function of the molecule up to the second order. With these constants and from the expressions for ν_3 and x_{33} in (87), Chap. III, and with due regard to (81), it is possible to calculate the values of ν_3 and x_{33} for the molecule $C^{13}O_2$ in which the carbon atom of mass 12 is replaced by the isotope of mass 13. The value of the expected observed frequency is found to be 2284.5 cm^{-1}. Recently Nielsen[11] has located and resolved a band at 2284.5 cm^{-1}. The agreement between the calculated and the observed frequencies thus points to the correctness of the explanation of the observed band and to the satisfactoriness of the potential function defined by (2) and (6).

2) CS_2

From the similarity of the sulphur and the oxygen atoms in their electron structure, one would expect the CS_2 molecule to have a structure similar to that of CO_2. Measurements of the permanent dipole moment of the molecule show that its value is zero and thus point to a symmetrical structure.[1] The data from the infrared and the Raman spectra, as summarized in the following table, are consistent with a linear symmetrical structure.

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[10] Because of some errors in the equations (87) as given in the paper of Adel and Dennison, Phys. Rev. 43, 716, (1933), the values of the potential constants given in their second paper, *ibid.*, 44, 99, (1933), are in error. The values given here are the corrected values. Account has not been taken, however, of the second-order correction mentioned on P. 139.

[11] A. H. Nielsen, Phys. Rev. 53, 983, (1938). The calculated frequency given in this paper is in error since it is based on the erroneous expressions and potential constants in the papers of Adel and Dennison.

[1] C. T. Zahn, Phys. Rev. 35, 848, (1930); C. H. Schwingel and J. W. Williams, Phys. Rev. 35, 855, (1930).

Transition $v_1\,v_2\,l\,v_3 \to$	$v_1\,v_2\,l\,v_3$	Infrared cm^{-1} obs.	Raman cm^{-1} obs.	Observers[2]
0 0 0 0	0 1 1 0	396.8 *Q*	400.5 (0.8)[3]	D. W.; V
	1 0 0 0		656.5 (0.15)	L. S. N.
	0 2 0 0		796.0 (0.18)	L. S. N.
	0 0 0 1	1523		B. C.
	1 0 0 1	2184		B. C.; S.
	0 2 0 1	2330		B. C.
0 1 1 0	1 1 1 0		648.3 ww	L. S. N.
	0 3 1 0		804.9 ww	L. S. N.
1 0 0 0	0 0 0 1	878		B. C.

Table VI. Vibrational spectrum of CS_2
Numbers in parentheses are the degrees of depolarization.

The infrared band at 396.8 cm^{-1} with a *Q* branch is the perpendicular fundamental ν_2. Its appearance in the Raman spectrum is probably due to the break-down of the selection rule as the result of the intermolecular forces in the liquid. The two strong lines at 656.5 and 796.0 cm^{-1} have been ascribed to transitions from the normal state to the pair of resonating levels $v_1=1$ and $v_2=2$, as in CO_2.[4] Their great intensities[5] and their low values for the degrees of depolarization exclude the possibility that the line 795.0 cm^{-1} may be purely due to the overtone $2\nu_2$. A first order calculation (Chap. III, §4, B) shows, however, that in this case the resonance between ν_1 and $2\nu_2$ is loose, the values Δ and $|b|$ being ca. 120 and 50 cm^{-1} respectively.[6]

For such a heavy molecule, the rotational line spacings are too small to be resolved, and the moment of inertia can not be obtained in this way. The C—S distance is found from electron diffraction measurements to be 1.54±0.03Å[7].

[2] D. W.=D. M. Dennison and N. Wright, Phys. Rev. 38, 2007, (1931); V.=S. Ventekateswaran, Phil. Mag. 15, 263, (1933); L. S. N.=A. Langseth, J. O. Sϕrensen & J. Rud Nielsen, Jour. Chem. Phys. 2, 402, (1934); B. C.=C. R. Bailey & A. B. D. Cassie, Proc. Roy. Soc. A 132, 236, (1931); 140, 605, (1933); S.=J. A. Sanderson, Phys. Rev. 50, 209, (1936).

[3] S. Bhagavantam, Ind. Jour. Phys. 7, 79, (1932); Phys. Rev. 39, 1020, (1932).

[4] E. Fermi, Zeits. f. Physik 71, 250, (1931).

[5] The relative intensities of the 656 and 796 cm^{-1} lines are 3.1:1 according to S. Pienkowski, Acta Phys. Polonica 1, 87, (1932).

[6] Langseth, Sϕrensen & Nielsen, *loc. cit.*; also D. M. Dennison, Phys. Rev. 41, 304, (1932).

[7] P. C. Cross and L. O. Brockway, Jour. Chem. Phys. 3, 821, (1935).

Because of the large mass of the S atoms, the corrections for anharmonicity of the vibrations are certainly negligible. On taking for the zeroth-order frequencies the observed values $\nu_1=660$, $\nu_2=397$, $\nu_3=1523$ cm^{-1}, one finds for the constants in the potential (3) the following values:

$$k = 7.55, \qquad k_1 = 0.67, \qquad k_\alpha = 0.24\times10^6,$$
$$r^2k_\alpha = 0.56\times10^{-11}\,\text{dy. cm./rad.} \qquad (7)$$

3) OCS (carbonyl sulphide)

The infrared spectrum of this molecule has been studied by Cassie and Bailey[1] and more recently in greater detail by Bartunek and Barker.[2] The Raman spectrum data are available from the work of Dadieu and Kohlrausch.[3] The classification of the observed frequencies is given in the following table.

Transition		Infrared		Raman	cm^{-1} calc.
$v_1v_2\,l\,v_3 \rightarrow$	$v_1v_2\,l\,v_3$	cm^{-1} obs. & type		cm^{-1} obs.	
0 0 0 0	0 1 1 0	* 521.5	$\perp$	524	*
	1 0 0 0	* 859.2	$\parallel$	859	*
	0 2 0 0	1047.4	$\parallel$	1041	1037.5
	1 1 1 0			1383	1380.7
	0 3 1 0	* 1558.6	$\perp$		*
	2 0 0 0	* 1710	$\parallel$		*
	1 2 0 0	* 1892	$\parallel$		*
	0 0 0 1	* 2050.5	$\parallel$	2055	*
	0 1 1 1	* 2575	$\perp$		*
	2 1 1 0			2233	2227
	1 0 0 1	* 2919	$\parallel$		*
	0 2 0 1	3096	$\parallel$		3094
	2 0 0 1 ?	3739	$\parallel$		3779
	0 0 0 2	* 4101	$\parallel$		*
0 1 1 0	0 2 0 0	514.3	$\perp$		516
0 1 1 0	0 2 2 0	* 526.6	$\perp$		*
0 1 1 0	0 0 0 1	1530.4	$\perp$		1529
0 2 0 0	2 0 0 0			678	672.5

Table VII. Vibrational spectrum of OCS

In this case the value 0.65×10^{-18} e.s.u. for the permanent electric moment[4] is of little help in deciding between the linear and the bent model for the molecule. On assuming, however, a linear model, the considerations of §2, A. Chap. IV, show that one may distinguish between the perpendicular and the parallel type bands with and without a Q branch respectively, and from considerations similar to those for the linear YX_2 molecule in Chap. III, §3, A, it follows that for the $\perp$ and the $||$ bands, $\Delta l = \pm 1$ and 0 respectively. It is seen from the above table that a classification of the observed bands can be made in accordance with these selection rules.

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[1] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. A 135, 375, (1932); Zeits. f. Phys. 79, 35, (1932).

[2] P. F. Bartunek and E. F. Barker, Phys. Rev. 48, 376, (1935).

[3] A. Dadieu and K. W. F. Kohlrausch, Phys. Zeits. 33, 165, (1932).

[4] C. T. Zahn and J. Miles, Phys. Rev. 32, 497, (1928).

From the bands marked by *, the anharmonicity coefficients in an energy expression of the form (73), Chap. III, can be calculated:

$$\begin{array}{llll} \nu_1 = 863.4, & x_{11} = -4.2, & x_{12} = -2.35, & \\ \nu_2 = 518.95, & x_{22} = -0.1, & x_{23} = 9.3, & x_{ll} = 2.65. \\ \nu_3 = 2050.5, & x_{33} = 0, & x_{13} = 3, & \end{array} \tag{8}$$

With these, the zeroth order frequencies are obtained from (75), Chap. III,

$$\omega_1 = 865.3, \qquad \omega_2 = 518.8, \qquad \omega_3 = 2042.9. \tag{9}$$

The constants in the potential

$$2V = k_1(\delta r_1)^2 + k_2(\delta r_2)^2 + 2k_3\,\delta r_1\,\delta r_2 + k_\alpha\,(s\delta\alpha)^2 \tag{10}$$

cannot be determined since there are only two parallel fundamentals but three constants k_1, k_2, k_3. On neglecting the interaction between the two extreme atoms by putting $k_3=0$, one obtains from (23), Chap. II,[5]

$$\begin{array}{ll} k_{CS} = 8.35, & k_{CO} = 13.4\times 10^5 \\ & k_\alpha s^2 = 0.635\times 10^{-11}\ \text{dy. cm/rad.} \end{array} \tag{11}$$

These C-O and C-S bond constants differ appreciably from their values in the CO_2 and CS_2 molecules.[6] Although the values in (11) should not be directly compared with those in (5) and (7) since we have neglected the term in k_3, the considerably stronger binding between the carbon and the oxygen atoms in CO_2 (force constant about 20 % greater than that in OCS) is indicative of a different electronic structure in these molecules. According to the theory of Pauling, the wave function of the normal state is a linear combination, in certain proportions, of the wave functions of the three states.[7] The greater binding in the C-O bond in CO_2 is due to the contributions of the wave functions for the triple bonds, while in OCS these contributions are considerably smaller.

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[5] This is calculated with the values C-O=1.16Å, C-S=1.56Å obtained from electron diffraction measurements by Cross and Brockway, Jour. Chem. Phys. 3, 821, (1935).

[6] Penney and Sutherland, Proc. Roy. Soc. A 156, 654, (1936), have calculated the potential constants for the CO_2, CS_2, OCS molecules as follows:

CO_2 : $k_{CO}=15.2\times 10^5$, $k_\alpha r^2 = 3.09\times 10^{-11}$
CS_2 : $k_{CS}= 7.6$, $k_\alpha r^2 = 2.22$
OCS: $k_{CO}=14.2$, $k_{CS} = 8.0\times 10^5$, $k_\alpha S^2 = 2.62\times 10^{-11}$

These values differ from the values given here because (i) we employ the zeroth order frequencies for CO_2 and OCS, and (ii) we include the cross term in the potential for CO_2 and CS_2. Because of an error, all their values for the deformation constant $k_\alpha S^2$ are too great by a factor 4.

4) N_2O

This molecule has the same number of electrons as CO_2 and has physical properties that are strikingly similar to those of CO_2. Its structure, however, is now definitely known to be linear but non-symmetrical, on the following evidences: (1) the permanent electric moment is not zero, but is $0.14 \pm 0.02 \times 10^{-18}$ e.s.u.,[1] (2) the rotational structure of the vibration-rotational bands is consistent with a linear but non-symmetrical model[2], (3) the vibrational spectrum does not show the operation of the selection rules for the linear symmetrical model which are found to hold strictly in the case of CO_2[3], (4) the presence of all the three fundamental frequencies in the Raman spectrum shows that the molecule must be nonsymmetrical,[4] and (5) an approximate theoretical estimate of the energies of the two forms N-N-O and N-O-N shows that the nonsymmetrical form is definitely more stable[5].

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[7] See Chap. III, §5, A.

[1] E. Czerlinsky, Zeits. f. Physik 88, 515, (1934).

[2] E. K. Plyler and E. F. Barker, Phys. Rev. 38, 1827, (1931). That the rotational lines are regularly spaced shows that the molecule must be linear. The absence of alternating intensities shows, however, that the molecule must be nonsymmetrical, since the symmetrical N—O—N would show an alternating intensity of 1:2 corresponding to the value 1 for the nuclear spin of the nitrogen atom.

D. Bender, Phys. Rev. 45, 732, (1934), also arrived at the same conclusion from the impossibility of resolving the rotational lines in the Raman spectrum of the molecule.

[3] Plyler and Barker, *loc. cit.*; see Table VIII below.

[4] S. Bhagavantam, Nature 127, 817, (1931); Ind. Jour. Phys. 6, 319, (1931); Dickenson, Dillon & Rasetti, Phys. Rev. 34, 582, (1929); A. Langseth and J. Rud Nielsen, Nature 130, 92, (1932).

[5] C. E. Sun & T. Y. Wu, Jour. Chin. Chem. Soc. 4, 340, (1936), found by the semi-empirical method of Eyring that the energies of the forms N—O—N and N—N—O are 144.6 and 197.6 Calories, while for the forms O—C—O and O—O—C they are 248.5 and 202.2 respectively. While the absolute values may be only very rough approximations, their relative values are believed to indicate the relative stabilities of the two forms for each molecule.

The infrared and the Raman spectrum data are summarized in the following table.

Transition $v_1 v_2 l v_3$	$\rightarrow$ $v_1 v_2 l v_3$	Obs. ν & band type		Calc. ν
0 0 0 0	0 1 1 0	589.0	$\perp$	*
	0 2 0 0	1167.3	$\parallel$	*
	1 0 0 0	1285.4	$\parallel$	*
	1 1 1 0	1868	$\perp$	1869.6
	0 0 0 1	2224.1	$\parallel$	*
	1 2 0 0	2462.2	$\parallel$	*
	2 0 0 0	2564.2	$\parallel$	*
	0 1 1 1	2799.1	$\perp$	2799.2
	0 2 0 1	3366.5	$\parallel$	*
	1 0 0 1	3482.2	$\parallel$	*
	0 0 0 2	4420.7	$\parallel$	*
	2 0 0 1	4736.0	$\parallel$	4733.7
0 1 1 0	0 2 0 0	579.5	$\perp$	578.3
	0 2 2 0	590.5	$\perp$	*
	1 2 2 0	1845	$\perp$	1866.4
	1 2 0 0	1829	$\perp$	1854
	0 2 0 1	2777	$\perp$	2777.4
	0 2 2 1	2786	$\perp$	2789.7
0 0 0 0	1 0 0 0	1283	Raman	1285.4
	0 0 0 1	2226	Raman	2224.1

Table VIII. Vibrational spectrum of N_2O

From the bands marked by *, the anharmonicity coefficients are obtained.

$$\begin{aligned} \nu_1 &= 1288.7, & x_{11} &= -\ 3.3, & x_{12} &= -\ 4.8, & & \\ \nu_2 &= \ 588.2, & x_{22} &= -\ 2.3, & x_{23} &= -12.5, & x_{ll} &= 3.1. \qquad (12) \\ \nu_3 &= 2237.8, & x_{33} &= -13.7, & x_{13} &= -26.1, & & \end{aligned}$$

From these, the zeroth-order frequencies can be calculated,

$$\omega_1 = 1309.8, \qquad \omega_2 = 601.5, \qquad \omega_3 = 2277.0, \qquad (13)$$

Just as in the case of OCS, the two parallel fundamentals do not suffice for the determination of the three constants k_1, k_2, k_3 in the potential (10). The assumption that $k_3=0$ leads to complex solutions for the constants k_1 and k_2. Following Rosenthal[6], we may obtain a rough estimate of these constants by assuming the smallest value of k_3 that gives real solutions for k_1 and k_2. The determinantal equation corresponding to the potential (10) gives the following relations

$$\lambda_1+\lambda_3=\frac{m_1+m_2}{m_1m_2}k_1+\frac{m_2+m_3}{m_2m_3}k_2-\frac{2}{m_2}k_3\,,$$

$$\lambda_1\cdot\lambda_3=\frac{m_1+m_2+m_3}{m_1m_2m_3}(k_1k_2-k_3^2)\,, \tag{14}$$

the relation for λ_2 being the same as in (23), Chap. II. One finds

$$k_{NN}\sim 14.3,\qquad k_{NO}\sim 15.3,\qquad k_3\sim 0.27\times 10^5,$$
$$k_\alpha s^2\simeq 0.63\times 10^{-11}. \tag{15}$$

In the calculation of $k_\alpha s^2$, the approximate N-N and N-O distances 1.09 and 1.21 Å respectively have been used, their exact values being undeterminable from the moment of inertia $I=66.0\times10^{-40}$ g.cm^2 obtained from the rotational line spacings in the vibration-rotational bands.[7,8]

5) HCN

The infrared and the photographic regions of the spectrum and also the Raman spectrum of this molecule have been investigated by a number of authors[1]. That the rotational lines in the vibration-rotational bands are regularly spaced shows that the molecule must be linear. The observed bands and their assignments are summarized in the following table.

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[6] Jenny E. Rosenthal, Jour. Chem. Phys. 5, 465, (1937). The constants calculated here differ from her values because she used the ν's instead of the zeroth order frequencies ω's in the calculation.

[7] The value for the moment of inertia given by Plyler and Barker, *loc. cit.*, is corrected by Barker, Phys. Rev. 41, 369, (1932).

[8] Maxwell, Mosley & Deming, Jour. Chem. Phys. 2, 331, (1934), obtained from electron diffraction measurements the value 2.88±0.05 Å for the distance between the two extreme atoms in N_2O. This distance together with $I=66.0\times10^{-40}$ gives, however, no real values for the N—N and N—O distances.

[1] C. B.=K. N. Choi & E. F. Barker, Phys. Rev. 43, 777, (1932); B=Barker, *ibid.*, 23, 200, (1924); A. B.=A. Adel & Barker, *ibid.*, 45, 277, (1934); B. B.=R. M. Badger & I. L. Binder, *ibid.*, 37, 800, (1931); K.=C. R. Kastler, C. R. 194, 858, (1932); B. L.=Brackett and Liddel, Smithonian Inst. 85, No. 5, (1931); L.=E Lindholm, Zeits. f. Physik 108, 454, (1938).

Transition $v_1\ v_2\ l\ v_3 \rightarrow v_1\ v_2\ l\ v_3$		Obs. ν & band type		Calc. ν	Observers[1]
0 0 0 0	0 1 1 0	712.3	⊥	*	C. B.
	0 2 0 0	1412.4	∥	*	C. B.
	1 0 0 0	2089.0	Raman	2092.5	K.
	0 3 1 0	2117.3	⊥	2113.3	B.
	1 1 1 0	2801.1	⊥	*	C. B.
	0 0 0 1	3312.9	∥	3313.8	A. B.
	0 1 1 1	4005.6	⊥	4006.5	A. B.
	2 1 1 0	4903.9	⊥	*	A. B.
	1 0 0 1	5395	∥	5391.9	A. B.
	0 0 0 2	6523.5	∥	6521.4	A. B.
	1 0 0 2	8585.6	∥	8584.8	B. L.; L.
	0 0 0 3	9627.2	∥	*	B. L.; L.
	1 0 0 3	11674.4	∥	11675.9	B. B.
	0 0 0 4	12635.8	∥	*	B. B.
	1 0 0 4	14670.7	∥	14669.9	L.
	0 0 0 5	15552.04	∥	*	L.
0 1 1 0	0 2 0 0	700	⊥	700.1	C. B.
	0 2 2 0	712	⊥	713.1	C. B.
	0 4 0 0	2087.7	⊥	2089.7	B.
	0 4 2 0	2102.7	⊥	*	B.
	0 1 1 3	9568.5	∥	*	L.
	1 1 1 3	11613.5	∥	*	L.
	0 1 1 4	12557.5	∥	12557.4	L.

Table IX. Vibrational spectrum of HCN

From the bands marked by *, the anharmonicity coefficients can be calculated to be

$$\begin{aligned} \nu_1 &= 2040.5, & x_{11} &= 52.0, & x_{12} &= -3.7, & & \\ \nu_2 &= 711.9, & x_{22} &= -2.85, & x_{13} &= -14.6, & x_{ll} &= 3.25, \\ \nu_3 &= 3368.6, & x_{33} &= -55.5, & x_{23} &= -19.6, & x_{333} &= 0.77. \end{aligned} \tag{16}$$

With these values, (75), Chap. III, give for the zeroth-order frequencies

$$\omega_1 = 1999.5, \qquad \omega_2 = 729.4, \qquad \omega_3 = 3450.0. \tag{17}$$

The value of the moment of inertia of the molecule has been given by Badger and Binder as 18.79×10^{-40} g.cm^2., by Choi and Barker as 18.68, by Bartunek and Barker as 18.72.[2] The H-C and the C-N bond distances can be calculated by combining this moment of inertia with that of the DCN molecule obtained also by Bartunek and Barker from the ν_2 fundamental (see below on DCN). The result is

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[2] P. F. Bartunek and E. F. Barker, Phys. Rev. 48, 516, (1935).

[3] Herzberg, Patat & Spink, Zeits. f. Physik 102, 1, (1936), gave $r(C-H) = 1.057$ and $r(C-N) = 1.154$Å. This C—H distance must replace the older value 1.08Å obtained by Hedfeld and Mecke, Zeits. f. Physik 64, 151, (1930), from the Raman spectrum obtained by Dickenson, Dillon and Rasetti, Phys. Rev. 34, 582, (1929). See section on C_2H_2 below.

$$r(\mathrm{C-H}) = 1.06\ \text{Å}, \qquad r(\mathrm{C-N}) = 1.15\ \text{Å}, \qquad (18)$$

Before a determination of the potential constants of the molecule, it is necessary to decide between the two possible structures

$$\mathrm{H:C}\,\vdots\vdots\,\mathrm{N:} \qquad\qquad \mathrm{H:}\overset{+}{\mathrm{N}}\,\vdots\vdots\,\overset{-}{\mathrm{C}}\,: \qquad (19)$$

From the Raman spectrum, Dadieu[4] found a very weak line at 2062 cm^{-1} in addition to the intense line at 2094 cm^{-1}. The weak line he ascribed to the second form in (19), on the basis of a comparison between the Raman spectra of aceto-nitrile $\mathrm{H_3C\text{-}CN}$ and of aceto-isonitrile $\mathrm{H_3C\text{-}NC}$. From the relative intensities of the 2094 and 2062 cm^{-1} lines, he concluded that ordinarily hydrocyanic acid consists of about 99.5% of the first form. This is supported by the infrared and the Raman data on the DCN molecule to be discussed below. More recently, Williams[5] found that there is a very weak band at 2020 cm^{-1} (4.95μ) beside the strong band at 2100 cm^{-1} (4.76μ) in the absorption spectrum of aqueous solution of hydrocyanic acid. The weak band is ascribed to the second form in (19), and its concentration is estimated at about 2% from the relative intensities of the two bands.

The constants in the zeroth order potential (10) can be calculated for various assumed values of the constant k_3 as follows:[6]

k_{CH}	k_{CN}	k_3	
6.30	16.2	0	
6.25	16.4	−0.3	
6.17	16.6	−0.6	(20)

and $$k_\alpha s^2 = 0.26\times10^{-11}\ \text{dy. cm./rad.}$$

A calculation of the constants in the most general cubic and quartic potential functions is as yet not possible as there are more unknown constants than there are relations among them. For this reason, it

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[4] A. Dadieu, Naturwiss. 18, 895, (1930); see also Kohlrausch, *Der Smekal-Raman Effekt*, Pp. 245, 319, 320, (§4, D below).

[5] D. Williams, Jour. Chem. Phys. 4, 84, (1936).

[6] It is to be noted that these force constants differ considerably from the values obtained by using instead of the zeroth-order frequencies the observed frequencies $\nu_1=2089$, $\nu_2=712$, $\nu_3=3313$, namely,

$$k_{CH}=5.7, \qquad k_{CN}=18.06 \ \text{for}\ k_3=-0.3.$$

See a similar situation in the case of C_2H_2 below; also T. Y. Wu & A. T. Kiang, Jour. Chem. Phys. 7, 178, (1939).

would be desirable to have a similar analysis of the spectrum of DCN, as it would furnish the necessary relations for this purpose.

5a) DCN

The Raman spectrum shows a strong line at 1906 cm^{-1} [1] and the infrared absorption spectrum shows two bands at 569.1 and 2630 cm^{-1}.[2] These are undoubtedly the fundamentals ν_1, ν_2, ν_3 of the molecule. The fundamental $\nu_2=569.1$ has been resolved into rotational lines. From the line spacing $\Delta\nu=2.414$ cm^{-1}, the value 22.92×10^{-40} g. cm^2 is obtained for the moment of inertia of the molecule.[3]

6, 7, 8) ClCN, BrCN, ICN

The Raman spectra of these molecules are known[1]. In such heavy molecules, the effect of anharmonicity will be small and in the calculation of the potentials we may take the observed frequencies as the zeroth-order frequencies. As the interaction between the two extreme atoms in such molecules probably cannot be neglected, and as the two parallel fundamentals do not suffice for the determination of the three constants in the potential (10), it would not be possible to obtain accurate values for the C-N and C-X bond constants. The results for $k_3=0$ are given in Table X together with the observed frequencies and the electron diffraction values for the C-Cl and C-Br distances[2].

	ν_1	ν_2	ν_3	$r(C-X)$	$k_\alpha s^2\times10^{11}$	$k_{C\text{-}N}$	$k_{C\text{-}X}$
ClCN	729	397	2201	1.67	0.40	16.6	5.15
BrCN	580	368	2187	1.79	0.37	16.8	4.17
ICN	470	321	2158	1.96	0.30	16.7	2.94

Table X. Fundamental frequencies & potential constants of halogen cyanides

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[1] A. Dadieu and H. Kopper, Wien. Anz. 92, (1935); *Landolt-Börnstein Tables*, Erg. III, P. 1194.

[2] P. E. Bartunek and E. F. Barker, Phys. Rev. 48, 516, (1935).

[3] An estimate of the zeroth-order frequencies can be made by means of equations (14) and the constants in (20) with $k_3=-0.3$. They are

$$\omega_1=1900, \qquad \omega_2=578, \qquad \omega_3=2600 \tag{21}$$

Comparison of these with the observed values shows that the effect of anharmonicity is smaller in DCN than in HCN.

[1] W. West & Marie Farnsworth, Jour. Chem. Phys. 1, 402, (1933).

[2] J. Y. Beach & A. Turkevich, Jour. Am. Chem. Soc. 61, 299, (1939). The C—N distance is given to be 1.13 Å. The C—I distance given in Table X is that estimated by D. P. Stevenson, Jour. Chem. Phys. 7, 171, (1939).

By varying the value of k_3 from -1×10^5 to 1×10^5, the values of the C-N bond constants in these molecules vary about the values in Table X to the extent of about 15%. As there seem to be no *a priori* reasons or convincing arguments for any particular value of k_3, we should perhaps regard the C-N constants as uncertain to the same extent. The electron diffraction values for the Cl-C and Br-C distances indicate some contributions of double bond characters arising from resonance between the structures $X-C\equiv N$ and $X=C=N$. This is also shown by a comparison of the C-X bond constants in these molecules and those in the methyl halides which contain single bond C-X (see Table L).

9, 10, 11) OCN^-, SCN^-, $SeCN^-$ ions

The Raman frequencies of these ions are known[1]. The constants in the simple valence force potential ($k_3=0$ in (10)) calculated from the observed frequencies are summarized in Table XI.

	ν_1	ν_2	ν_3	$k_{CN}\cdot10^{-5}$	$k_{CX}\cdot10^{-5}$	$k_\alpha s^2\cdot10^{11}$
OCN^-	857		2193	16.57	4.69	
SCN^-	750	398	2066	14.35	5.34	0.36
$SeCN^-$	575		2052	14.64	4.14	

Table XI. Fundamental frequencies and potential constants of OCN^-, SCN^-, $SeCN^-$ ions.

In the calculation of $k_\alpha s^2$ for SCN^-, the C-N distance is taken to be 1.15Å and the S—C distance 1.54Å. It is seen that the C—N bond constants in SCN^- and $SeCN^-$ are considerably lower (by about 15%) than the value in HCN, and the difference seems to be somewhat greater than what can be ascribed to the neglect of the interaction between the two extreme atoms. It is possible that the difference, if it is real, is due to a difference in the structure of the C—N bonds in these ions and the HCN molecule[2].

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[1] Langseth, J. Rud Nielsen & Sørensen, Zeits. f. phys. Chem. B 27, 100, (1934); Cf. L. Kahovec and K. W. F. Kohlrausch, Zeits. f. phys. Chem. B 37, 421, (1937).

[2] J. W. Linnett and H. W. Thompson, Jour. Chem. Soc. Lond. P. 1399, (1937), suggested that there is a resonance between the structures $S=C=N^-$ and $S^-—C\equiv N$ since the C—S bond constant lies between the value 7.55 in CS_2 (in which the bond is mainly a double bond) and the value 3.0 in methylthiol in which it is a single bond.

B) Bent Molecules

1) H_2O

The water molecule is of great interest because of its common occurrence and also because in spite of its apparant simplicity, it possesses a rich spectrum extending from the far infrared to the photographic region. The near infrared absorption bands have been studied by Sleator and Plyler[1], the photographic bands by Mecke and his collaborators[2], and the far infrared region by Randall, Dennison and their collaborators[3]. The complexity of the rotational structure of the bands confirms the triangular model for the molecule suggested by chemical and electric moment data and demanded by the quantum theory of directed valence. Such a molecule belongs to the class of asymmetrical rotators discussed in Chap. IV. In Chap. III, (94a) and (94b), we have shown that in transitions in which Δv_3 is $\left\{\begin{matrix}\text{even}\\ \text{odd}\end{matrix}\right.$, the change of the electric moment is $\left\{\begin{matrix}\parallel\\ \perp\end{matrix}\right.$ to the axis of symmetry. This axis of symmetry is the axis of least or intermediate moment of inertia according as

$$\tan^2\frac{\alpha}{2} \lessgtr \frac{M}{M+2m} \tag{22}$$

where α is the apex angle of the triangular molecule, and M, m are the masses of the oxygen and the hydrogen atom respectively. According to §3, C and Fig. 20 in Chap. IV, vibration-rotational bands with $\Delta v_3 = \left\{\begin{matrix}\text{even}\\ \text{odd}\end{matrix}\right.$ will be of the $\left\{\begin{matrix}\text{“}B\text{”}\\ \text{“}A\text{”}\end{matrix}\right.$ or the $\left\{\begin{matrix}\text{“}A\text{”}\\ \text{“}B\text{”}\end{matrix}\right.$ type according as $\alpha \lessgtr 88\frac{1}{2}^\circ$. In particular, the two fundamentals ν_1 and ν_2 will be of the "*A*" type and ν_3 of the "*B*" type if $\alpha < 88\frac{1}{2}^\circ$, and conversely if $\alpha > 88\frac{1}{2}^\circ$. An examination of the band structure of the fundamentals and the harmonic and combination bands shows that the latter is the case, *i.e.*, the axis of the least moment of inertia is perpendicular to the axis of symmetry of the molecule. In fact, Mecke and his collaborators have been able to give a complete analysis of all the bands in the near infrared and the photographic region (17 bands altogether) on the basis of the quantum mechanics of an asymmetrical rotator. They located all the rotational energy levels for $J \leqq 4$, and some of the levels for $J > 4$. From these energy levels, it is possible to calculate the principal moments of inertia of the molecule for different vibrational states by means of the equations giving the energies according to the quantum mechanics. They found that the effective moments of inertia vary for different vibrational states, their values in 10^{-40} g.cm^2 being expressible by the following empirical relations

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[1] W. W. Sleator, Astrophys. Jour. 48, 125, (1918); Sleator and E. R. Phelps, *ibid.*, 62, 28, (1925); E. K. Plyler and Sleator, Phys. Rev. 37, 1433, (1931); Plyler, *ibid.*, 39, 77, (1932).

[2] R. Mecke, Zeits. f. Physik 81, 313, (1933); W. Baumann and Mecke, *ibid.*, 81, 445, (1933); Freundenberg and Mecke, *ibid.*, 81, 465, (1933); Mecke, *Hand-u. Jahrbuch d. chem.* Physik 9/II, P. 365, (1934).

[3] H. M. Randall, D. M. Dennison, N. Ginsberg & L. R. Weber, Phys. Rev. 52, 160, (1937); also R. B. Barnes, W. S. Benedict & C. M. Lewis, *ibid.*, 47, 918, (1935); N. Wright and Randall, *ibid.*, 44, 39, (1933).

$$\begin{aligned} I_A &= 0.996 - 0.026\, v_1 - 0.098\, v_2 + 0.045\, v_3, \\ I_B &= 1.908 + 0.033\, v_1 - 0.034\, v_2 + 0.014\, v_3, \\ I_C &= 2.981 + 0.062\, v_1 + 0.062\, v_2 + 0.047\, v_3, \end{aligned} \tag{23}$$

in which the terms 0.996, 1.908, 2.981 are the values in the normal state. That the values of I_A, I_B, I_C do not satisfy the relation $I_C = I_A + I_B$ for a plane model is due to the fact that the values so obtained are the effective average values during the vibrations. The dimensions of the molecule in the normal state calculated from the moments of inertia are the following:[4]

$$\alpha = 104^\circ\, 36', \qquad r\,(\mathrm{O-H}) = 0.9558\ \text{Å}, \tag{24}$$

With improved experimental technique, Randall, Dennison and their collaborators have recently mapped and accounted for practically every line $J, \tau \rightarrow J', \tau'$ of observable intensity in the pure rotational spectrum in the region between 80 and 550 cm^{-1}. The accuracy with which tbe frequencies of the lines are determined is about 0.05 cm^{-1}. The rotational energy levels derived from the analysis of the spectrum are given in Table XII for $J \leqq 6$, just to give some idea as to the arrangement and the magnitude of the rotational levels of an asymmetrical rotator. It is worthy of remark that the observed frequencies of 160 lines all agree within 3 or 4 tenths of a cm^{-1} with the frequencies calculated from 115 rotational levels (of which those in Table XII are only a part). In general, for states with low values of J and τ, the rotational levels obtained empirically agree within *ca.* 1 cm^{-1} with those calculated from the quantum-mechanical theory for the asymmetrical rotator with the dimensions given in (24); but for states with high values of J and τ, they differ by as much as 200 cm^{-1} for $J=10$ and $\tau=10$ and by *ca.* 280 cm^{-1} for $J=11$ and $\tau=11$. These differences can be accounted for by taking into consideration the effect of the centrifugal distortion of the molecule. Hence we may say that our knowledge concerning the vibrational and the rotational energies of the water molecule is now fairly complete.

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[4] The quantum theory of directed valence requires the angle between the two O—H bonds to be a right angle. The greater value observed can be explained as arising from the exchange repulsion between the two H atoms.

Table XIII summarizes the vibration-rotational bands of the water molecule in the infrared and the photographic region, together with their assignments and the values of the valence angle for the upper vibrational states. The letters D and Z under "band type" denote that the band is of the "*B*" type (no apparent Q branch) and the "*A*" type (with an apparent Q or zero branch) respectively.

J	τ	E in cm^{-1}	J	τ	E in cm^{-1}	J	τ	E in cm^{-1}
0	0	0	4	−4	221.90	5	4	742.30
			4	−3	224.74	5	5	742.30
1	−1	23.78	4	−2	275.21			
1	0	37.06	4	−1	300.33	6	−6	446.69
1	1	42.30	4	0	315.66	6	−5	447.20
			4	1	382.49	6	−4	542.80
2	−2	70.03	4	2	383.90	6	−3	553.00
2	−1	79.38	4	3	488.24	6	−2	602.78
2	0	95.04	4	4	488.24	6	−1	649.11
2	1	134.81				6	0	661.63
2	2	136.10	5	−5	325.23	6	1	756.90
			5	−4	326.49	6	2	757.84
3	−3	136.74	5	−3	399.45	6	3	888.85
3	−2	142.17	5	−2	416.02	6	4	888.89
3	−1	173.33	5	−1	446.52	6	5	1045.34
3	0	206.25	5	0	503.94	6	6	1045.34
3	1	212.07	5	1	508.86			
3	2	285.26	5	2	610.21			
3	3	285.45	5	3	610.42			

Table XII. Rotational energy levels of H_2O

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[5] D. H. Rank, Jour. Chem. Phys. 1, 504, (1933); D. H. Rank, K. D. Larsen and E. R. Bordner, Jour. Chem. Phys. 2, 464, (1934). Lines at 1648, 984 cm^{-1} reported by Johnston and Walker, Phys. Rev. 39, 535, (1932) were not confirmed by Rank.

Transitions $v_1\ v_2\ v_3 \longrightarrow v_1\ v_2\ v_3$		cm^{-1} obs.	band type	cm^{-1} calc.	α
0 0 0	0 1 0	1595.4	*D*	*	107° 30′
	0 2 0	3152	*D*	*	110° 10′
	1 0 0	3654	Raman[5]		
	0 0 1	3756.35	*Z*	*	103° 45′
	0 1 1	5332.3	*Z*	5331.0	106° 30′
	1 0 1	7253	*Z*	7255	103° 45′
	1 1 1	8807.0	*Z*	8810.6	105° 30′
	2 0 1	10613.1	*Z*	*	103° 40′
	0 0 3	11032.36	*Z*	*	102° 5′
	2 1 1	12151.14	*Z*	12150	105° 40′
	0 1 3	12565.01	*Z*	*	104° 10′
	3 0 1	13830.92	*Z*	*	103° 20′
	1 0 3	14318.77	*Z*	*	102° 20′
	3 1 1	15347.9	*Z*	15338.6	105° 25′
	1 1 3	15832.47	*Z*	*	104° 20′
	3 2 1	16821.21	*Z*	16827.4	107° 25′
	4 0 1	16899.01	*Z*	16908.1	103° 55′
	2 0 3	17495.48	*Z*	17464.7	102° 0′

Table XIII. Vibrational spectrum of H_2O

Bonner has carried out a first and second order perturbation calculation of the vibrational energy of the water molecule[6]. The energy is expressible in the form

$$E_v/h = x' + \nu_1 v_1 + \nu_2 v_2 + \nu_3 v_3 + x_{11} v_1^2 + x_{22} v_2^2 + x_{33} v_3^2$$

$$+ x_{12} v_1 v_2 + x_{13} v_1 v_3 + x_{23} v_2 v_3, \tag{25}$$

and the zeroth-order frequencies are given by

$$\begin{aligned} \omega_1 &= \nu_1 - x_{11} - \tfrac{1}{2} x_{12} - \tfrac{1}{2} x_{13}, \\ \omega_2 &= \nu_2 - x_{22} - \tfrac{1}{2} x_{12} - \tfrac{1}{2} x_{23}, \\ \omega_3 &= \nu_3 - x_{33} - \tfrac{1}{2} x_{13} - \tfrac{1}{2} x_{23}, \end{aligned} \tag{26}$$

where the ν's and the x's are expressible in terms of the constants in the anharmonic potential. From the nine bands marked by * in Table XIII, the following coefficients are obtained

$$\begin{aligned} \nu_1 &= 3674.8, & x_{11} &= -70.2, & x_{23} &= -21.0, \\ \nu_2 &= 1615.0, & x_{22} &= -19.5, & x_{12} &= -18.9, \\ \nu_3 &= 3796.0, & x_{33} &= -39.5, & x_{13} &= -106.1. \end{aligned} \tag{27}$$

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[6] L. G. Bonner, Phys. Rev. 46, 485, (1934).

and from (26),

$$\omega_1 = 3807.5, \qquad \omega_2 = 1654.5, \qquad \omega_3 = 3899.0. \tag{28}$$

For the zeroth-order potential of the molecule, Cross and Van Vleck suggested a modified valence potential of the form[7]

$$2V = k\left[(\delta r_1)^2 + (\delta r_2)^2\right] + k_\alpha (r\delta\alpha)^2 + 2k_1\delta r_1\delta r_2 + 2k_2(\delta r_1 + \delta r_2) r\delta\alpha. \tag{29}$$

With this potential, the determinantal equation gives

$$\begin{aligned} \lambda_1 + \lambda_2 &= (k+k_1)\left(\frac{1}{\mu} + \frac{\cos\alpha}{M}\right) + 2k_\alpha\left(\frac{1}{\mu} - \frac{\cos\alpha}{M}\right) - \frac{4k_2}{M}\sin\alpha, \\ \lambda_1 \cdot \lambda_2 &= \frac{M+2m}{Mm^2}\left[2k_\alpha (k + k_1) - 4\,k_2^2\right], \\ \lambda_3 &= (k-k_1)\left(\frac{1}{\mu} - \frac{\cos\alpha}{M}\right), \end{aligned} \tag{30}$$

where $\mu = mM/(M+m)$. On neglecting the term in k_2, one can calculate the other three constants with the frequencies in (28),[8]

$$\begin{aligned} k = 8.23, \qquad k_\alpha = 0.75, \qquad k_1 &= -0.076 \times 10^6, \\ k_\alpha r^2 &= 0.68 \times 10^{-11} \text{ dy.cm./rad.} \end{aligned} \tag{31}$$

A calculation of the first and the second order potentials of Bonner is as yet not practicable since the number of unknown constants exceeds the number of relations connecting them and the cefficients in (25). For this purpose, a vibrational analysis of the spectrum of the D_2O molecule would be necessary.

Finally we may remark in passing that the water molecule plays an important part in the "blanket" effect of the atmosphere of the earth[9]. The intense absorption band ν_2 of the molecule gives rise to a strong absorption by the water vapor in the atmosphere in the region from 5 to 8μ. At still longer wave length, $\lambda > 17\mu$, strong absorption arises from the pure rotational spectrum of the water molecule. These together with the strong $\nu_2 = 667$ cm^{-1} (15μ) fundamental of CO_2 and the $\nu_1=1037$ cm^{-1} (9.6μ) and $\nu_2=710$ cm^{-1} (14μ) fundamentals of ozone account for the blanket effect of the atmosphere for infrared radiations beyond 5μ.

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[7] P. C. Cross and J. H. Van Vleck, Jour. Chem. Phys. 1, 350, (1933).

[8] This value for the O—H bond constant is to be compared with the value 7.45×10^5 obtained by using the observed frequencies instead of the zeroth-order frequencies.

[9] A. Adel, V. M. Slipher & E. F. Barker, Phys. Rev. 47, 580, (1935).

1a) D_2O

The fundamental frequencies ν_2 and ν_3 of this molecule have been located in the infrared absorption spectrum at 1179 and 2784 cm^{-1} respectively by Sleator and Barker[1]. The fundamental ν_1 has been found in the Raman spectrum of the vapor at 2665 cm^{-1}.[2] An analysis of the pure rotational spectrum has recently been started in the Michigan laboratory[3]. But there seem to have been no observations on the harmonic and combination bands that would permit a calculation of the zeroth-order frequencies of the molecule[4]. This is due to the impracticability of obtaining a large amount of the heavy water vapor for the harmonic and combination bands to show with observable intensities (especially in the photographic region which in the case of H_2O contains a large number of bands in the absorption spectrum of the atmosphere of the solar radiations).

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[1] W. W. Sleator & E. F. Barker, Phys. Rev. 46, 337, (1934); Jour. Chem. Phys. 3, 660, (1935).

[2] D. H. Rank, K. D. Larsen & E. R. Bordner, Jour. Chem. Phys. 2, 464, (1934); R. W. Wood, Phys. Rev. 45, 392, 732, (1934).

[3] N. Fuson, H. M. Randall & D. M. Dennison, Phys. Rev. 55, 590, (1938).

[4] On the reasonable assumption that the potential of D_2O is the same as in H_2O, the zeroth-order frequencies of D_2O can be calculated from (30). They are

$$\omega_1=2764.7, \qquad \omega_2=1209.7, \qquad \omega_3=2865.4. \tag{32}$$

Bonner, Phys. Rev. 46, 458, (1934), has made an estimate of the expected observed frequencies on the following considerations: Because of the relation (58), Chap. III, between the normal coordinates and the dimensionless coordinates, namely, $y_i=2\pi\sqrt{(\omega i/h)}X_i$, it is seen from the expressions for the second-order energy change (70), (71) and (72) of Chap. III, that the anharmonicity coefficients in D_2O would be to those in H_2O approximately as $(\omega')^2$ to $(\omega)^2$. From (28) and (32), one finds $(\omega'/\omega)^2\simeq0.532$ and hence

$$\begin{array}{lll} \nu_1=2694, & x_{11}=-37.7, & x_{23}=-11.3, \\ \nu_2=1188, & x_{22}=-10.5, & x_{12}=-10.1, \\ \nu_3=2810, & x_{33}=-21.2, & x_{13}=-56.9. \end{array} \tag{33}$$

The expected observed frequencies are

$$\nu_1+x_{11}=2656, \qquad \nu_2+x_{22}=1178, \qquad \nu_3+x_{33}=2789 \tag{34}$$

in good agreement with the observed values.

[1] D. R. Rank, K. D. Larsen & E. R. Bordner, Jour. Chem. Phys. 2, 464, (1934); R. W. Wood, Phys. Rev. 45, 732, (1934), gave 2674 for HDO vapor and 2601 for D_2O vapor.

1b) HDO

The fundamental ν_1 has been located at 2718 cm^{-1} in the Raman spectrum of the vapor[1], and only the fundamentals ν_1 and ν_2 have been observed in the infrared, at 2720 and 1403 cm^{-1} respectively[2]. The values calculated by Van Vleck and Cross by employing the constants for H_2O in the potential (29) are $\nu_1=2720$, $\nu_2=1400$ and $\nu_3=3750$[3]. The Raman and the absorption spectra of the liquid have been studied by a number of authors,[4] but the liquid frequencies differ in general too much from the frequencies of the gas to be considered in the calculation of the potential function of the molecule.[5]

2) H_2S, 2a) HDS, 2b) D_2S

From the similarity between the sulphur and the oxygen atoms, one expects the structure of the H_2S molecule to be similar to that of the H_2O molecule. The study of the vibrational spectrum of H_2S shows that this is in fact the case. The infrared and the Raman spectra of H_2S,[1]

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[2] E. F. Barker and W. W. Sleator, Jour. Chem. Phys. 3, 660, (1935).

[3] J. H. Van Vleck and P. C. Cross, Jour. Chem. Phys. 1, 357, (1933).

[4] J. W. Ellis & B. W. Sorge, Phys. Rev. 45, 757, (1934), gave $\nu_1=2530$ cm^{-1} (3.95μ), $\nu_2=1480$ cm^{-1} (6.76μ), $\nu_3=3280$ cm^{-1} (3.05μ). The much lower values for the O—H valence frequency is probably due to association. L. B. Borst, A. M. Buswell & W. H. Rodebush, Jour. Chem. Phys. 6, 61, (1938), found $\nu_1=2689$ cm^{-1} and $\nu_3=3659$ cm^{-1} in solution of HDO in CCl_4 and CS_2. These values are quite close to the gas frequency and the calculated frequency respectively. This disappearance of the liquid frequencies upon solution in CCl_4 is similar to that observed for alcohol by Errera, Trans. Faraday Soc. 32, 122, (1937), and is due to the breaking up of the associated molecules.

[5] L. Herzberg, Zeits. f. Physik 107, 549, (1937), observed and analyzed a band at 1.161μ which was ascribed to $\nu_1+2\nu_2+\nu_3$. From the rotational analysis, the following constants were obtained: $r(O-H)=0.970$; $r(O-D)=0.948A$; $\alpha=105°43'$.

[1] A. H. Rollefson, Phys. Rev. 34, 604, (1929), 1260 cm^{-1} band under low dispersion; H. H. Nielsen & E. F. Barker, *ibid.*, 37, 727, (1931), 2630 and 3790 cm^{-1} bands under high dispersion; H. H. Nielsen and A. D. Spraque, *ibid.*, 37, 1183, (1931); Spraque and Nielsen, *ibid.*, 43, 375, (1933), 5135 cm^{-1} band; Spraque and Nielsen, Jour. Chem. Phys. 5, 85, (1937), 1290 and 2685 cm^{-1} bands under high dispersion; P. C. Cross, Phys. Rev. 46, 536, (1934); 47, 7, (1935), 9911 and 10100 cm^{-1} bands in the photographic region and rotational analysis of the 9911 cm^{-1} band; Cross, Jour. Chem. Phys. 5, 370, (1937), 9911 cm^{-1} band; B. L. Crawford and Cross, *ibid.*, 5, 371, (1937), discussions; C. R. Bailey, H. W. Thompson & J. B. Hale, *ibid.*, 4, 625, (1936), 1236, 2423, 2632, 2911, 3794, 5155 cm^{-1} bands all under low dispersion; S. Bhagavantam, Nature 126, 502, (1930), 2615 cm^{-1} in the Raman spectrum of H_2S gas; G. M. Murphy & J. E. Vance, Jour. Chem. Phys. 6, 426, (1938), 2610.8 cm^{-1} in the Raman spectrum of the gas.

HDS,[2] D_2S[3] have been investigated by a number of authors. The complexity of the rotational structure of the bands leaves no doubt that the H_2S molecule belongs to the class of asymmetrical rotators. From an analysis of the rotational structure of the photographic band at 9911 cm^{-1}, Cross has been able to obtain the values of the principal moments of inertia of H_2S, namely,

$$I_A = 2.667, \qquad I_B = 3.067, \qquad I_C = 5.845 \times 10^{-40}\,\mathrm{g.cm}^2. \tag{35}$$

The dimensions of the molecule, however, are not uniquely determined by these moments of inertia alone; in fact, there are two values for the apex angle, namely,

$$\alpha = 85°20' \quad \text{or} \quad 92°20' \tag{36}$$

that are both consistent with the above values of the moments of inertia. According to (22), the molecule will have its symmetry axis along the axis of least moment of inertia if the angle has the value 85° 20′, but along the axis of intermediate moment of inertia if $\alpha = 92° 20'$. It should be possible to decide between these two models from the rotational structure of the fundamental bands of the molecule. Unfortunately, the present state of our knowledge of the structure of the bands is such that a definite conclusion as to the value of the apex angle still cannot be made. Until more experimental data on the rotational structure of the bands are available, it does not seem advisable to decide on either one of these models. In the following, we shall rather summarize the empirical results obtained by different authors and their interpretations.

Let us first consider H_2S. The Raman frequency of the gas at 2611 cm^{-1} is most probably ν_1, as the corresponding vibration in H_2O is the only frequency observed in the Raman spectrum of the vapor. Its non-appearance in the absorption spectrum is also similar to the case of H_2O. The absorption spectrum has been studied by Bailey, Thompson and Hale under low dispersion (prism technique) and by Nielsen, Spraque and Barker under high dispersion (grating instrument). These authors agree in assigning the low frequency band at *ca.* 1250 cm^{-1} to ν_2 and the high frequency band at *ca.* 2650 cm^{-1} to ν_3, but disagree somewhat as to the values to be ascribed to the band centers, as seen in Table XIV. Nielsen and his collaborators found that the 1290 cm^{-1} band possesses an apparent Q branch while the 2685 cm^{-1} band is of the doublet type. It follows from §3, C, Chap. IV, and Fig. 20 that the axis of least moment of inertia must lie along the axis of symmetry of the molecule. This leads to the acute angle in (36) for the molecule.

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[2] Bailey, Thompson & Hale, *loc. cit.*, low dispersion study of HDS bands, see Table XV; A. H. Nielsen and H. H. Nielsen, Jour. Chem. Phys. 5, 277, (1937), 1090 cm^{-1} band under high dispersion.

[3] Bailey, Thompson & Hale, *loc. cit.*, 898, 1940, 2798 cm^{-1} bands under low dispersion; Nielsen & Nielsen, *loc. cit.*, 934, 2000, 2685 cm^{-1} bands under high dispersion; Murphy and Vance, *loc. cit.*, 1891.6 cm^{-1} in the Raman spectrum of D_2S gas.

Assignment	Nielsen, Sprague, & Nielsen			Bailey, Thompson, & Hale
	Obs. ν	Type	Δ	Obs. ν
ν_2	1290	Z	10	1236
ν_1	2610.8	Raman		2610.8
ν_3	2685	D	9	2632
$\nu_1+\nu_2$	3790	Z	10	
$2\nu_2$				2423
$\nu_2+\nu_3$				3794
$\nu_1+\nu_3$	5130	D		
$2\nu_1$				5156
$3\nu_1+\nu_3$				9911
$\nu_1+3\nu_3$				10100
$3\nu_1+2\nu_2$	9911	Z		
$2\nu_1+2\nu_3$	10100	Z		
?				2911

Table XIV. Vibrational spectrum of H_2S
Numbers under Δ are the average rotational line spacings.

Assignment	D_2S				HDS			
	Nielsen & Nielsen			Bailey *et al*	Nielsen & Nielsen			Bailey *et al*
	ν		Δ		ν		Δ	
ν_2	934	Z	4.8	898	1090	D	6.85	1078
ν_1	1891.6	Raman		1891.6				
ν_3	2000	D	5.0	1940				
$\nu_1+\nu_2$	2685	Z	5.0					2938
$2\nu_2$								2110
$\nu_2+\nu_3$				2798				3724
$2\nu_1$								3849
?								988

Table XV. Vibrational spectra of D_2S and HDS

On the other hand, from a comparison of the observed intensities of the lines in the Q branch ($J, \tau = J \longleftrightarrow J, \tau = J-1$) of the 9911 cm^{-1} band and the theoretical intensities obtained on considerations of the symmetry properties of the rotational levels, Cross concluded that the axis of least moment of inertia lies in a direction perpendicular to the symmetry axis.[4] This would lead to the value 92° 20′ for the apex angle. It seems that one can reconcile this result with that of Nielsen and his coworkers only by assuming that either the insufficiently resolved rotational structure in the infrared studies might have given a misleading impression as to the existence or absence of a *Q* branch, or the moments of inertia might change quite appreciably during the vibrations (see (23) for H_2O) so that the band structure might differ from what should be the case for a rigid molecule with $\alpha = 92° \; 20'$. It seems that this point must be settled by a complete rotational analysis of the infrared bands as for the H_2O molecule.

For D_2S, the Raman spectrum of the gas gives only one line at 1891.6 cm^{-1}, and infrared spectrum gives three bands. For HDS, only infrared data are available. The frequencies ascribed to the band centers by Bailey, Thompson and Hale again differ slightly from those by Nielsen and Nielsen, as seen in Table XV. As the observations of Bailey *et al* are made with low dispersion (no resolution into rotational lines) while those of the Nielsen's are made with much higher dispersion and resolution (rotational lines partially resolved), it seems that more weight should be given to the work of the latter authors. According to them, the observed band type of the bands again is consistent with the 85° 20′ for the apex angle, in contradiction to the conclusion of Cross. Again further experimental work and analysis of these bands are necessary before a definite assignment of the bands and a determination of the shape of the molecule can be made.

Because of the unsettled state as to the values and the assignments of the observed frequencies as discussed above, it seems rather premature to calculate the potential constants of the molecules H_2S, HDS, D_2S. We give below, however, the tentative values of the potential constants in (29) according to both Nielsen's assignment and that of Bailey, *et al.*[5]

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[4] The symmetry properties of the rotational levels are of two classes: one whose rotational wave function is symmetrical and spin wave function antisymmetrical with respect to the interchange of the two H nuclei, and the other with wave functions having reciprocal properties. As shown in Chap. IV, §3, transitions between levels of the first class have a factor 1 and those between levels of the second class a factor 3 in their intensities. A detailed consideration of the rotational wave function of the asymmetrical rotator YX_2 (Dennison, Rev. Mod. Phys. 3, 280, (1931)) shows that the symmetry properties are different for the two cases: axis of least moment of inertia $\parallel$ or $\perp$ to the symmetry axis. Hence from the observed intensities of the rotational lines, it is possible to distinguish between these two cases.

	According to Nielsen, *et al* $\alpha=85^\circ\ 20'$		According to Bailey, *et al* $\alpha=92^\circ\ 20'$	
	H_2S	D_2S	H_2S	D_2S
k_{HS}	4.02	4.19	4.25	4.33
k_α	0.48	0.49	0.476	0.478
k_1	-0.12	-0.27	-0.04	-0.07

Table XVI. Potential constants of H_2S and D_2S

It is seen that both assignments gave practically the same force constants. It must be remembered that these force constants are only approximate because (*i*) of the uncertainty in the value of the apex angle, (*ii*) of the uncertainties in the frequencies ascribed to the band centers, and (*iii*) of the fact that in our calculation according to Nielsen's assignment, the observed rather than the zeroth order frequencies have been used. Until the uncertainties due to (*i*) and (*ii*) have been removed, we must refrain from attempting any refinement of the calculation as done for the H_2O molecule.[6]

3) H_2Se, 3a) HDSe, 3b) D_2Se

The Raman spectrum of H_2Se gives one line at 2312 cm^{-1} and that of D_2Se one line at 1665 cm^{-1}.[1] The infrared spectra of the three

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[5] Bailey, Thompson & Hale, Jour. Chem. Phys. 4, 625, (1936), also calculated the potential constants for a model with $\alpha=110^\circ$. This value for α was obtained on what they called the Teller relation

$$\nu_1^2 H\left(S+2D\sin^2\frac{\alpha}{2}\right)=\nu_1'^2\, D\left(S+2H\sin^2\frac{\alpha}{2}\right)$$

between the symmetrical frequencies ν_1 of H_2S and D_2S. But this is obviously a mistake, since this relation holds for the antisymmetrical frequency ν_3 but not for ν_1, as can easily be seen from equs. (30) above. Also it has been pointed out by Spraque and Nielsen, *ibid.*, 5, 85, (1937), that the value $\alpha=110^\circ$ is entirely incompatible with the observed rotational structure of the bands.

[6] Bailey, Thompson & Hale, *loc. cit.*, have attempted to evaluate the coefficients in the expression (25) and to obtain the zeroth-order frequencies from (26). On account, however, of the uncertainty in the frequencies of the band centers determined from their low dispersion work, one may doubt the significance of the result of such a calculation.

[1] A. Dadieu and W. Engler, Wien. Anz. 128, (1935).

molecules have recently been observed by Sears, Cameron and Nielsen.[2] The frequencies and the rotational line spacings of the observed bands are summarized below.

	H_2Se		$HDSe$		D_2Se	
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
ν_1	2312 Ra.				1665 Ra.	
	2300 D	7.8	1610 Z			
ν_2	1100 D	7.8	910 D	5.5	760	4.0
ν_3	2380 Z	7.8	2385 D	5.5	1700	

Table XVII. Fundamental frequencies of H_2Se, HDSe, D_2S

A tentative calculation of the potential constants in (29) can be made with the data $\nu_1=2300$, $\nu_2=1100$, $\nu_3=2380$ for H_2Se and $\nu_3=1700$ for D_2Se. One obtains

$$\alpha \simeq 126^\circ$$

$$k_{HSe} = 3.18, \qquad k_\alpha = 0.35, \qquad k_1 = -\,0.09 \tag{37}$$

A check of these values is furnished by comparing the observed frequencies of HDSe with the values calculated by using these constants in (21) of Chap. II, which hold for $k_1=0$. The agreement is satisfactory. The constants in (37) are, however, only approximate, since an accurate calculation requires a knowledge of the zeroth-order frequencies of these molecules.

4) ClO_2

The infrared spectrum of this molecule has been studied by Bailey and Cassie[1] and by Ku.[2] The latter author found from the electronic bands that the fundamental frequencies of the normal electronic state are 954, 1105 and 529 cm^{-1}. The first two have been located in the infrared by all the above authors, but the last has not been observed in the infrared probably because of the limitation of the prism technique in their work. In table XVIII, we give Ku's assignment of the frequencies and her values for the constants in a simple valence force potential. In view of the general empirical result that in all other known

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[2] W. C. Sears, D. M. Cameron & H. H. Nielsen, Phys. Rev. 53, 830, (1938).

[1] Bailey and Cassie, Proc. Roy. Soc. A 137, 622, (1932); 140, 605; 142, 129, (1933).

[2] Z. W. Ku, Phys. Rev. 44, 376, (1933).

Obs. ν & band type	According to Ku	Here suggested
954 *D*	ν_2 *D*	ν_1 *D*
1105 *Z*	ν_3 *Z*	ν_3 *Z*
1884 ?	$2\nu_3$ *Z*	$2\nu_1$ *D*
2034 ?	$\nu_2+\nu_3$ *D*	$\nu_1+\nu_3$ *Z*
529 (from electronic band only)	ν_1 *Z*	ν_2 *D*
k_{ClO}	6.74×10^5	6.83×10^5
k_α	1.16	0.68
α	65°	122°

Table XVIII. Vibrational spectrum and potential constants of ClO_2

triatomic molecules the frequencies ν_1 and ν_3 which are essentially determined by the valence force are of the same order of magnitude and $\nu_3 > \nu_1$, and ν_2 is lower than both ν_1, and ν_3, it seems that an alteration of the assignment is desirable. This assignment leads to the value 122° for the apex angle and slightly different values for the constants. The value 137°±15° obtained from electron diffraction measurements seems to support this assignment.[3] An examination of the 529 cm^{-1} band, if it is a fundamental band at all, would decide between the two assignments.[4]

5) SO_2

The infrared spectrum of the SO_2 molecule has been studied by Bailey and Cassie,[1] and the Raman spectrum by a number of authors.[2] The triangular model is established by (*i*) the electron diffraction measurements of Cross and Brockway who found $r(S-O)=1.45\pm.02$Å and 124°±15° for the apex angle α,[3] (*ii*) the presence of three fundamentals in both the Raman and the absorption spectra, and (*iii*) the polarization characters of the Raman lines observed by Cabannes and Rousset.[2] The observed data are summarized in Table XIX.

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[3] Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

[4] It should be possible to discriminate between the two sets of constants in Table XVIII by comparing the observed isotope shifts in the molecules with Cl=35 and Cl=37 with the theoretical values according to the results of §7, Chap. II. The isotope shifts measured by Ku, *loc. cit.*, are, however, not sufficiently accurate for this purpose.

[1] Bailey and Cassie, Proc. Roy. Soc. A 130, 144, (1930); 137, 622; 138, 531; (1932); 140, 605, (1933); R. M. Badger and L. G. Bonner, Phys. Rev. 43, 305, (1933).

[2] Cf. Kohlrausch, *Der Smekal-Raman Effekt*, P. 352; J. Cabannes and A. Rousset, C. R. 194, 79, 707, (1932): H. Gerding & W. J. Nijveld, Rec. trav. chim. 56, 968, (1937).

Assignment	Obs. ν		and band type
ν_2	525		
	525	p	Raman (liquid)
ν_1	1150		*D*
	1151	p	Raman (gas)
ν_3	1360		*Z*
	1366	d	Raman (liquid)
$\nu_2+\nu_3$	1870		?
$2\nu_1$	2305		*D*
$\nu_1+\nu_3$	2500		?

Table XIX. Vibrational spectrum of SO_2

With the fundamentals in Table XIX, and with $\alpha \simeq 122°$, the constants in the potential (29) can be calculated,

$$k_{SO} = 9.91, \qquad k_\alpha = 0.82, \qquad k_1 = -\ 0.09\times 10^5, \qquad k_\alpha\, r^2 = 1.73\times 10^{-11}. \tag{38}$$

6) NO_2

The infrared spectrum of this molecule has been investigated by a number of authors[1-4]. From electron diffraction measurements, it is established that the molecule is not linear and that the apex angle is ca. 120° and the N–O distance ca. 1.15A.[6] The dispersion employed in the infrared studies is low, except in the work of Sutherland who showed the 648, 2220 and 2910 cm^{-1} bands to be of the doublet type. The assignments of the observed bands have been recently discussed by Sutherland and Penney.[7] They are given in the following table.

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[3] P. C. Cross and L. O. Brockway, Jour. Chem. Phys. 3, 821, (1935); Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

[1] R. Schaffert, Jour. Chem. Phys. 1, 507, (1933), found also two bands at 1373 and 3008 cm^{-1}.

[2] G. B. B. M. Sutherland, Proc. Roy. Soc. A 145, 278, (1934), found in addition a band at 1360 cm^{-1} which he ascribed to the nitrite ions formed on the rocksalt windows of the absorption tube.

[3] Bailey and Cassie, Nature 131, 239, (1933).

[4] L. Harris, & G. W. King, Jour. Chem. Phys. 2, 51, (1934). They also calculated the anharmonicity coefficients in the energy expression. In view of the low accuracy with which the frequencies are known and of the lack of knowledge of the band types, the result is not included.

[6] Maxwell, Moseley & Deming, Jour. Chem. Phys. 2, 331, (1934). The experimental data do not entirely exclude the possibility that $\alpha=90°$.

Assignment	Obs. ν			Predicted type	Observers
	cm^{-1}		type		
ν_2	648	s	*D*	*D*	1, 2
ν_1	1321	w	?	*D*	5
ν_3	1621	s	?	*Z*	1, 2
$\nu_2+\nu_3$	2220	m	*D*	*Z*	2
$2\nu_1$	2630	m	?	*D*	2, 5
$\nu_1+\nu_3$	2910	s	*D*	*Z*	2, 4
$2\nu_3$	3242	m	?	*D*	2, 4
$\nu_1+\nu_2+\nu_3$	3597	w	?	*Z*	4
$2\nu_1+\nu_3$	4140	s	?	*Z*	4
$3\nu_3$	4753	m	?	*Z*	4
	3927	w	?		4
	4427	w	?		4

Table XX. Vibrational spectrum of NO_2

The assignment of the 1321 cm^{-1} frequency to ν_1 is based on the observation by Harris, Benedict and King[6] of the appearance of the frequency differences 1321 and 2630 cm^{-1} in the ultraviolet spectrum of the molecule. That the frequency 1321 cm^{-1} has not been observed in the infrared may be due (*i*) to its low intensity—a situation similar to that of the H_2O spectrum, and (*ii*) to the fact that it might have been masked by the strong absorption at 1350-1370 cm^{-1} which has been ascribed to the nitrite ions formed on the rocksalt windows of the absorption cell.[2] An examination of the Raman spectrum would be desirable to definitely establish the fundamental 1321 cm^{-1}, although this would not be without experimental difficulty as the spectrum must be taken at temperatures higher than $\sim$150°C in order to rid the gas of N_2O_4.

It is seen from Table XX that the predicted band types of the 2220 and 2910 cm^{-1} bands do not agree with the observed structure. Sutherland and Penney suggested that this may be due to the unsuitable experimental conditions for the observation of the expected Q branches, or to the possibility that these bands may not belong to NO_2 at all (the 2220 cm^{-1} band may be the N_2O fundamental ν_3). In any case, until more data are available, the assignments in Table XX must be regarded as tentative.

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[7] Sutherland and W. G. Penney, Proc. Roy. Soc. A 156, 678, (1936). The value $\nu_1=1370$ given in a paper preceding this by the same authors appears to be an error on comparison with the second paper.

[6] Harris, Benedict & king, Nature 131, 621, (1933).

The constants in the potential (29) can be calculated, on assuming $\alpha=120°$,

$$k_{NO} = 9.38, \qquad k_\alpha = 1.08, \qquad k_1 = -0{,}23, \qquad k_\alpha r^2 = 1.43 \times 10^{-11}. \tag{39}$$

7) O_3 (ozone)

The infrared spectrum has been investigated by Gerhard and by Hettner and his ccworkes.[1] The assignment of the observed frequencies has been discussed by a number of authors.[2] Although an equilateral triangle model can be eliminated since for such a model there would be one (doubly degenerate) active fundamental while the the observed spectrum calls for more than one, there has been considerable difficulty in assigning the observed frequencies and in determining the actual shape of the molecule, *i.e.*, the apex angle of the isoceles triangle model. It is shown by Sutherland and Penney[2] that the only assignment yielding reasonable values for the potential constants is the one shown in Table XXI, any other alternative assignment leading to unreasonably high values for the deformation force constant k_α.

Assignment	Observed			Predicted type
	cm^{-1}	int,	type	
ν_2	710	s	*D*	*D*
ν_1	1043,7	s	*D*	*D*
ν_3	1740	w	?	*Z*
$3\nu_2$	2105	s	?	*D*
$2\nu_1+\nu_2$	2800	w	?	*D*
$3\nu_1$	3050	w	?	*D*

Table XXI. Vibrational spectrum of O_3

This assignment leads to the following values for the apex angle and the constants in the simple valence force potential

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[1] S. L. Gerhard, Phys, Rev. 42, 622, (1932); Hettner, Pohlmann & Schumacher, Zeits. f. Physik 91, 372, (1934); Zeits. f. Elektrochem. 41, 524, (1935); A. Adel, V. M. Slipher & O. Fouts, Phys. Rev. 49, 288, (1936).

[2] R. M. Badger & L. G. Bonner, Phys. Rev. 43, 305, (1933); W. S. Benedict, *ibid.*, 43, 580, (1933); Hettner *et al, loc, cit.*; Sutherland and Penney, Proc. Roy. Soc. A 156, 678, (1936).

[3] G. Sutherland & S. L. Gerhard, Nature 130, 241, (1932).

$$\alpha \sim 127^\circ, \qquad k = 11.5, \qquad k_\alpha = 0.70 \times 10^5. \qquad (40)$$

It is seen from Table XXI that this assignment has the disadvantage of ascribing the weak band at 1740 cm^{-1} to the fundamental ν_3 which is strong in other triangular molecules such as H_2O, H_2S and NO_2. Although this may not be a series difficulty, the assignment must be regarded as tentative until the band types of the other absorption bands are known from further experiments. An observation of the Raman spectrum would be particularly valuable for establishing the fundamental frequencies, but an attempt by Sutherland and Gerhard to obtain the Raman spectrum has not yielded positive results.[3]

8) F_2O, 9) Cl_2O

Electron diffraction measurements show that these molecules are not linear but are symmetrical.[1] The bond distances and valence angles are as follows:

$$F_2O, \qquad r(F-O) = 1.41 \pm .05\ \text{Å}, \qquad \alpha = 100^\circ \pm 3^\circ$$

$$Cl_2O, \qquad r(Cl-O) = 1.68 \pm .03\ \text{Å}, \qquad \alpha = 115^\circ \pm 4^\circ, \qquad (41)$$

The infrared spectrum of F_2O has been studied by Hettner and his coworkers[2] and that of Cl_2O by Bailey and Cassie.[3] Sutherland and Penney[4] showed that the only assignments of the existing data that give reasonable values for the potential constants are the following:

Assignment	F_2O	Band type		Assignment	Cl_2O	Band type	
	cm^{-1}	obs.	pred.		cm^{-1}	obs.	pred.
ν_2	492	?	*D*	$2\nu_2$	640	?	*D*
$\nu_3 - \nu_2$	625	?	*Z*	ν_1	680	?	*D*
ν_1	833	*D*?	*D*	ν_3	973	Z	*Z*
$2\nu_2$	926	*D*	*D*	$\nu_2+\nu_3$	1245	?	*Z*
ν_3	1110	?	*Z*	$2\nu_1$	1331	?	*D*
$\nu_1+\nu_2$	1280	?	*D*				
$\nu_1+2\nu_2$	1740	*D*?	*D*				
$2\nu_3$	2190	?	*D*				
$2\nu_1+2\nu_2$	2544	?	*D*				

Table XXII. Vibrational spectra of F_2O and Cl_2O

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[1] Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

[2] Hettner, Pohlmann & Schumacher, Zeits. f. Physik 96, 203, (1935).

[3] Bailey and Cassie, Proc. Roy. Soc. A 142, 129, (1933).

[4] Sutherland and Penney, Proc. Roy. Soc. A 156, 678, (1936).

With the apex angles given in (41) and the fundamentals in Table XXII, the equations (30) with $k_2=0$ give no real solutions for k and k_1. On letting $k_1=0$ and regarding α as unknown, then one obtains[5]

$$\begin{aligned} &F_2O, \quad \alpha \sim 136^\circ, \quad k = 5.6, \quad k_\alpha = 0.58\times 10^5, \\ &Cl_2O, \quad \alpha \sim 132^\circ, \quad k = 5.0, \quad k_\alpha = 0.42\times 10^5. \end{aligned} \tag{42}$$

These values, and the assignments, must be regarded as tentative.

10) NOCl

The infrared spectrum of this molecule has been examined by Bailey and Cassie.[1] The dimensions of the molecule are known from electron diffraction measurements which give[2]

$$r(N-Cl) = 1.95\pm.01, \quad r(N-O) = 1.14\pm.02, \quad r(O-Cl) = 2.65\pm.01,$$
$$\angle ONCl = 116^\circ\pm 2^\circ.$$

The usual assignment of the fundamental frequencies $\nu_1=1832$, $\nu_2=633$, $\nu_3=923$ was found by Beeson and Yost to lead to too low a value for the entropy compared with the observed value (too low by 3.6 cal/mole per degree).[3] They suggested that the 923 cm^{-1} band is the combination of the 633 fundamental and a low frequency fundamental at 290 cm^{-1}. With $\nu_1=1832$, $\nu_2=290$, $\nu_3=633$, the discrepancy between the calculated and the observed entropies is only 0.3 cal/degree.

§2. Tetratomic Molecules

A) Linear Molecules

1) C_2H_2

The structure of this molecule is now known to be a linear and symmetrical one from a vast amount of spectroscopic data. Before discussing the experimental results, let us first examine the type of spectra to be expected of such a model.

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[5] R. Pohlmann & H. J. Schumacher, Zeits. f. Physik 100, 678, (1936), made the assignments: F_2O, $\nu_1=870$, $\nu_2=1280$, $\nu_3=1740$; Cl_2O, $\nu_1=658$, $\nu_2=973$, $\nu_3=1245$, and obtained the force constants F_2O, $k=13.5$, $k_\alpha=7.6$; Cl_2O, $k=13.5$ and $k_\alpha=7.6\times 10^5$.

[1] Bailey and Cassie, Proc. Roy. Soc. A 145, 336, (1934).

[2] Ketelaar, & Palmer, Jour. Am. Chem. Soc. 59, 2629, (1937).

[3] C. M. Beeson & D. M. Yost, Jour. Chem. Phys. 7, 44, (1939).

On a consideration of the "symmetry coordinates", it can readily be shown that of the 7 degrees of freedom for vibrations, 3 involve motions of the atoms along the axis and are called the parallel or valence vibrations, and 2 involve motions ⊥ to the axis and are called the perpendicular or deformation vibrations. As the motion of the atoms is isotropic in planes ⊥ to the axis of symmetry, each of the ⊥ vibrations is doubly degenerate. Of the 3 parallel vibrations, 2 are symmetrical and one antisymmetrical with respect to the center of symmetry; of the 2 ⊥ vibrations, one is symmetrical and one antisymmetrical with respect to the center.[1] The forms of the normal vibrations are shown in Fig. 25.

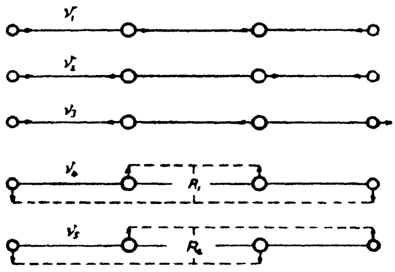

Fig. 25. Normal vibrations of linear symmetrical Y_2X_2

To obtain the normal frequencies of the molecule, the problem can be simplified by treating separately the parallel and the perpendicular vibrations, since there is no mechanical coupling between them and the electrical coupling is probably very small and negligible in the initial approximation.[2] For the parallel vibrations, let the changes in the H–C, C–C, C–H bond distances x_1, x_2, x_3 be chosen as the generalized coordinates. The kinetic energy is then[3]

$$2T = \frac{m(2M+m)}{S}(\dot{x}_1^2+\dot{x}_3^2)+\tfrac{1}{4}S\,\dot{x}_2^2+m\,(\dot{x}_1+\dot{x}_3)\dot{x}_2+\frac{2m^2}{S}\,\dot{x}_1\dot{x}_3, \tag{43}$$

where $S=2(M+m)$. The most general quadratic potential energy is

$$2V = k_1(x_1^2+x_3^2)+k_2x_2^2+2k_3(x_1+x_3)\,x_2+2k_4\,x_1x_3. \tag{44}$$

The determinantal equation separates into a quadratic and a linear factor for the symmetrical and antisymmetrical vibrations respectively,

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[1] These statements follow from considerations similar to those given for the YX_2 and Y_2X_4 models in Chap. II, §2.

[2] By mechanical and electrical couplings are meant the cross terms in the velocities and coordinates in the kinetic energy and the potential energy respectively.

[3] W. F. Colby, Phys. Rev. 47, 388, (1935). Note a misprint in the expression for λ_5 which is corrected here in (49) below.

$$\lambda_1 + \lambda_2 = \frac{1}{\mu}(k_1 + k_4) + \frac{2}{M}(k_2 - 2k_3),$$

$$\lambda_1 \cdot \lambda_2 = \frac{2}{mM}\left[(k_1 + k_4)k_2 - 2k_3^2\right],$$

$$\lambda_3 = \frac{1}{\mu}(k_1 - k_4), \tag{45}$$

where $\mu = mM/(M+m)$. The forms of the vibrations can be obtained by studying the normal coordinates Q_1, Q_2, Q_3 given by

$$x_i = \sum_k c_{ik} Q_k: \tag{46}$$

in which

$$c_{1\alpha} = A_\alpha \left[(\tfrac{1}{4}S\lambda_\alpha - k_2)\left\{\frac{m(2M+m)}{S}\lambda_\alpha - k_1\right\} - (\tfrac{1}{2}m\lambda_\alpha - k_3)^2\right],$$

$$c_{2\alpha} = A_\alpha \left[-(\tfrac{1}{2}m\lambda_\alpha - k_3)(\frac{2mM}{S}\lambda_\alpha - k_1 + k_4)\right],$$

$$c_{3\alpha} = A_\alpha \left[(\tfrac{1}{2}m\lambda_\alpha - k_3)^2 - (\tfrac{1}{4}S\lambda_\alpha - k_2)(\frac{m^2}{S}\lambda_\alpha - k_4)\right],$$

where $\alpha = 1, 2, 3$ and the A's are constants. On account of (45),

$$c_{11} = c_{31}, \quad c_{12} = c_{32}, \quad c_{13} = -c_{33}, \quad c_{23} = 0. \tag{47}$$

It follows from these that the forms of the vibrations are as shown in Fig. 25.

For the perpendicular vibrations, Colby chose the angles between two neighboring bonds as the generalized coordinates. The quadratic potential is

$$2V = k_\alpha(\alpha_1^2 + \alpha_2^2) + 2k'_\alpha \alpha_1 \alpha_2. \tag{48}$$

The determinantal equation gives

$$\lambda_4 = \frac{M+m}{mMa^2}(k_\alpha + k'_\alpha), \quad \lambda_5 = \frac{1+4c+4c^2+(M/m)}{Ma^2}(k_\alpha - k'_\alpha), \tag{49}$$

where a and b are the C—H and the C—C bond distance respectively and $c = a/b$. The forms of the vibrations can perhaps more conveniently be obtained by employing instead of the angles α_1 and α_2 the coordinates R_1 and R_2 defined by

$$\begin{aligned} 2R_1 &= (y_1 + y_4) - (y_2 + y_3), \\ 2(a+b)R_2 &= b(y_1 - y_4) + (2a+b)(y_3 - y_2), \end{aligned} \tag{50}$$

where y_1, y_2, y_3, y_4 are the displacements of the H, C, C, H atoms perpendicular to the axis, (Fig. 25). The kinetic energy is then

$$2T = \mu_1 \dot{R}_1^2 + \mu_2 \dot{R}_2^2 \tag{51}$$

where

$$\mu_1 = 2mM/(M+m), \quad \mu_2 = 2mM(a+b)^2/[Mb^2 + (2a+b)^2 m].$$

The potential energy which must be even in both R_1 and R_2 is

$$2V = C_1 R_1^2 + C_2 R_2^2. \tag{52}$$

It is seen that the R's are proportional to the normal coordinates

$$Q_4 = \sqrt{\mu_1}\, R_1, \qquad Q_5 = \sqrt{\mu_2}\, R_2 . \tag{53}$$

The equations (49) giving the frequencies become then

$$\lambda_4 = \frac{C_1}{\mu_1}, \qquad \lambda_5 = \frac{C_2}{\mu_2} . \tag{49a}$$

The selection rules for the fundamental vibrations follow immediately from the symmetry properties of the vibrations. They are:

	ν_1	ν_2	ν_3	ν_4	ν_5	
Infrared	inactive	inactive	$\parallel$	$\perp$	inactive	(54)
Raman	p	p	inactive	inactive	*d*	

where the $\parallel$ and the $\perp$ type bands have rotational structures described in Chap. IV, § 2, A.

To account for the harmonic and combination bands, it is necessary to consider the deviation of the potential energy from the quadratic potentials (44) and (48). This effect of anharmonicity gives rise to harmonic and combination bands for which the selection rules have been given in (95), Chap. III, and depend only on the symmetry of the molecule and the potential but are independent of the numerical values of the constants in the potential. To obtain the vibrational energy of the molecule, however, the anharmonic potential must be known. Recently, Wu and Kiang[4] have carried out a perturbation calculation of the energy change produced by the most general cubic and quartic potentials consistent with the symmetry of the molecule. It is shown that the energy is expressible in the form

$$E/h = x_0 + \sum_1^5 \nu_i v_i + \sum_1^5 x_{ii} v_i^2 + \tfrac{1}{2} \sum_{\substack{ij \\ i \neq j}} x \, v_i \, v_j + \sum_1^2 x_{l_i l_i} \, l_i^2 \tag{55}$$

in which the coefficients ν's and *x's* are constants expressible in terms of the zeroth order frequencies and the constants in the anharmonic potentials. From the 22 expressions for these coefficients, one obtains

$$\begin{aligned}
\omega_1 &= \nu_1 - x_{11} - \tfrac{1}{2}x_{12} - \tfrac{1}{2}x_{13} - \phantom{\tfrac{1}{2}}x_{14} - x_{15} \\
\omega_2 &= \nu_2 - x_{22} - \tfrac{1}{2}x_{12} - \tfrac{1}{2}x_{23} - \phantom{\tfrac{1}{2}}x_{24} - x_{25} \\
\omega_3 &= \nu_3 - x_{33} - \tfrac{1}{2}x_{13} - \tfrac{1}{2}x_{23} - \phantom{\tfrac{1}{2}}x_{34} - x_{35} \\
\omega_4 &= \nu_4 - 2x_{44} - \tfrac{1}{2}x_{14} - \tfrac{1}{2}x_{24} - \tfrac{1}{2}x_{34} - x_{45} \\
\omega_5 &= \nu_5 - 2x_{55} - \tfrac{1}{2}x_{15} - \tfrac{1}{2}x_{25} - \tfrac{1}{2}x_{35} - x_{45}
\end{aligned} \tag{56}$$

These relations enable one to obtain the zeroth order frequencies when the coefficients ν's and *x's* have been determined from an analysis of the vibrational spectrum of the molecule.

On account of (56), there are only 17 independent relations connecting the coefficients ν*'s* and *x's* and the constants in the anharmonic potentials (25 in number in the most general potentials). The theory of interactions between vibrations and rotations of the molecule leads to an expression of the form (97), Chap. IV, for the rotational lines of a band arising from a transition from the normal state to the state v_1, v_2, v_3, v_4, l_1, v_5, l_2.[5] The values of the α's determined from the rotational structures of 5 appropriate bands will furnish 5 more relations for the constants in the cubic anharmonic potential.

In the following, we give an analysis of the spectrum of the acetylene molecule on the basis of the above normal coordinate method, which in the case of the CO_2 molecule has been found highly successful[6].

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[4] T. W. Yu and A. T. Kiang, Jour. Chem. Phys. 7, 178, (1939).

[5] T. Y. Wu, to appear in Jour. Chem. Phys.

The infrared spectrum of C_2H_2 has been studied by Levin and Meyer[7] and the photographic region has been thoroughly investigated by Mecke[8], Herzberg[9], Funke[10] and their collaborators. The Raman spectrum of C_2H_2 in both the gaseous and the liquid state has been examined by a number of workers[11]. Both the photographic and the infrared bands show that (*i*) they consist of regularly spaced rotational lines characteristic of linear molecules, (*ii*) there are two types of bands, namely, those with and without the *Q* branch, corresponding to the parallel and the perpendicular bands discussed in §2, Chap. IV, and the selection rules (82) of Chap. III, and (*iii*) the rotational lines show the alternating intensities discussed in §3, Chap. IV, the value 1:3 corresponding to the spin ½ of the hydrogen nucleus. The alternating intensities establish beyond doubt that the molecule is symmetrical. Herzberg and Funke[9] observed a few bands which do not show the alternating intensities, and the explanation is that they arise from transitions from a state in which one of the perpendicular fundamentals ν_4 and ν_5 has already been excited. This is seen to be so on considerations similar to those leading to (69), Chap. IV, for the CO_2 molecule, and is established by their measurements of the intensities of the bands at different temperatures of the absorbing gas.

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[6] Recently, R. Mecke and Ziegler, Zeits. f. Physik 101, 405, (1936), have treated the spectrum of C_2H_2 on the basis of Mecke's method, Zeits. f. Physik 99, 217, (1936), which has been described in Chap. III, §3, B. They treated the two C—H valence vibrations as two degenerate vibrations, and similarly for the two deformation vibrations. They found that their equations, together with two empirically determined coefficients, satisfactorily account for most of the observed bands. It has been pointed out by Childs and Jahn, Zeits. f. Physik 104, 804, (1937), however, that the agreement between the observed and the calculated frequencies involving the deformation vibrations is entirely accidental, it being obtained through the error of a sign, and that the inability of the theory to include the interaction term $k'_{\alpha}\alpha_1\alpha_2$ in (48) in the perturbation calculation leads to the result that $\nu_4 < \nu_5$, in contradiction with the observed values $\nu_4 = 729$ and $\nu_5 = 612$ cm^{-1}. Apart from this criticism, it is not easily understandable why Mecke's method, which neglects all the mechanical and electrical couplings in the initial approximation and includes only mechanical couplings in the next approximation, can be essentially superior to the normal coordinate method which takes into account all the mechanical and part of the electrical couplings in the initial approximation and the effect of anharmonicity up to the second approximation. For these reasons, we prefer the normal coordinate treatment, although Mecke's result will also be included in Table XXIII below.

[7] A. A. Levin and C. F. Meyer, Jour. Am. Opt. Soc. 16, 137, (1928).

[8] R. Mecke, Leipziger Vorträger, (1931); K. Hedfeld & R. Mecke, Zeits. f. Physik 64, 151, (1930); Mecke, *ibid.*, 64, 173, (1930); Hedfeld & P. Lueg, *ibid.*, 77, 446, (1932); W. Lochte-Holtgreven & E. Eastwood, *ibid.*, 79, 450, (1932); Mecke & Ziegler, *loc. cit.*

[9] G. Herzberg & J. W. T. Spink, Zeits. f. Physik 91, 386, (1934); G. Funke and Herzberg, Phys. Rev. 47, 100, (1936).

[10] G. Funke, Zeits. f. Physik 99, 341, (1936); 104, 169, (1937); Funke and E. Lindholm, *ibid.*, 106, 518, (1937).

[11] S. Bhagavantam & A. V. Rao, Proc. Ind. Acad. Sci. A 3, 135, (1936), C_2H_2 gas; Jour. Chem. Phys. 4, 293, (1936), comments on the interpretation of Glockler and Morrell; G. Glockler & E. Morrell, *ibid.*, 4, 15, (1936), C_2H_2 liquid; Glockler & M. M. Renfrew, *ibid.*, 6, 340, (1938), C_2H_2 liquid and summary of previous work.

The Raman spectrum of C_2H_2 in the gaseous state consists of two intense lines at 1973 and 3371 cm^{-1} and a weak doublet at 589 and 643 cm^{-1}. The first two are due to the totally symmetrical vibrations ν_1 and ν_2. The doublet is explained as the *O, P* and *R, S* branches of the band due to ν_5 at *ca.* 616 cm^{-1}. Another very weak line at 1233 cm^{-1} is probably due to $2\nu_5$. The Raman spectrum of the liquid shows the above lines at slightly displaced frequencies and in addition a weak line at 1934 cm^{-1}. Glockler and Renfrew attribute this line to the molecule $H-C\equiv C^{13}-H$. An approximate calculation of the expected isotope shift from equations (45) shows that $\Delta\nu \sim -38$ cm^{-1}, in agreement with the observed value.

The assignment of the absorption bands presents a more difficult problem. Sutherland[12] gave the assignments of some 20 bands known up to that time. Herzberg and Spink[13] later proposed another classification which differs from Sutherland's chiefly in interchanging the assignments $3\nu_3=9835$ and $\nu_3+2\nu_2=9640$ cm^{-1}. Still later, Mecke and Ziegler[6] gave a classification based on the perturbation theory of Mecke. In view of the more recent extensive observations of Funke and Lindholm, the original analysis of Herzberg and Spink does not seem satisfactory, as the calculated frequencies differ from the observed values by *ca.* 30 cm^{-1} for most of the bands. A redetermination of the coefficients in (55) according to their classification can be made, and in fact good agreement between the observed and the calculated frequencies can be obtained for all except for five or six bands.[14] In Table XXIII, we give the classification of Mecke and Ziegler, the modified one of Herzberg and Spink, and the one proposed by Wu and Kiang which is based on an extension of that of Sutherland.

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[12] G. B. B. M. Sutherland, Phys. Rev. 43, 883, (1933).

[13] Herzberg and Spink, *loc. cit.*, see also Funke, Zeits. f. Physik 99, 341, (1936).

[14] See a forthcoming paper of T. Y. Wu in Jour. Chem. Phys. (1940).

Table XXIII. Vibrational spectrum of C_2H_2

Observed			Wu-Kiang		Modified Herzberg-Spink		Mecke-Ziegler	
cm^{-1}		B′	$v_1v_2v_3v_4v_5l_1l_2$	calc.	$v_1v_2v_3$ $v_4v_5l_1l_2$	calc.	v_{CH} v_{CC} δ_{CH}	calc.
3288	‖		0 0 1 0 0 0 0	*		*	$1_1\ a\ 0\ 0$	3281
3372	Raman		0 1 0 0 0 0 0	*		*	$1_1\ s\ 0\ 0$	3374
6500	‖		0 1 1 0 0 0 0	6513		6548	$2_2\ a\ 0\ 0$	6554
9640	‖	1.1585	0 2 1 0 0 0 0	*	0030000	*	$3_3\ a\ 0\ 0$	9638
12675	‖	1.1510	0 3 1 0 0 0 0	12670	0130000	*	$4_4\ a\ 0\ 0$	12678
15600	‖	1.1435	0 4 1 0 0 0 0	*	0050000	*	$5_5\ a\ 0\ 0$	15600
18430	‖	1.1358	0 5 1 0 0 0 0	18133	0150000	18414	$6_6\ a\ 0\ 0$	18124
1973	Raman		1 0 0 0 0 0 0	*		*	$0\ \ 1\ 0$	1973
5250	‖		1 0 1 0 0 0 0	*		5257	$1_1\ a\ 1\ 0$	5246
9835	‖	1.1579#	0 0 3 0 0 0 0	*	0210000	*	$3_1\ a\ 0\ 0$	9832
11783	‖	1.1514	1 0 3 0 0 0 0	11781	1210000	11793	$3_1\ a\ 1\ 0$	11781
8512	‖		1 1 1 0 0 0 0	8474		8512	$2_2\ a\ 1\ 0$	8511
11600	‖	1.1526	1 2 1 0 0 0 0	*	1030000	*	$3_3\ a\ 1\ 0$	11587
14617	‖	1.1492#	1 3 1 0 0 0 0	14624	1130000	14627	$4_4\ a\ 1\ 0$	14619
17519	‖	1.1386	1 4 1 0 0 0 0	17552	1050000	17551	$5_5\ a\ 1\ 0$	17533
13532	‖	1.147	2 2 1 0 0 0 0	13534	2030000	*	$3_3\ a\ 2\ 0$	13526
612	Raman		0 0 0 0 1 0 0	*		*	$0\ \ 0\ 1_1\ s$	
729	⊥		0 0 0 1 0 1 0	*		*	$0\ \ 0\ 1_1\ a$	
1328.6	‖		0 0 0 1 1 1 1	*		*	$0\ \ 0\ 2_0\ a$	1328
4690	‖		0 1 0 1 1 1 1	4680		4681	$1_1\ s\ 0\ 2_0\ a$	4680
3882	⊥		0 0 1 0 1 0 1	*		3884	$1_1\ a\ 0\ 1_1\ s$	3882
4092	⊥		0 1 0 1 0 1 0	*		*	$1_1\ s\ 0\ 1_1\ a$	4092
10365	⊥	1.1587	0 1 2 1 0 1 0	*		*	$3_3\ s\ 0\ 1_1\ a$	10351
10413.5	⊥	1.158	0 0 3 0 1 0 1	10391	0210101	10411	$3_1\ a\ 0\ 1_1\ s$	10409
13230	⊥	1.150	0 3 1 0 1 0 1	*	0130101	13230	$4_4\ a\ 0\ 1_1\ s$	13240
3295	‖		1 0 0 1 1 1 1	3286		3288	$0\ \ 1\ 2_0\ a$	3287
9906	‖	1.162	1 2 0 1 1 1 1	*	?		$2_0\ s\ 1\ 2_0\ a$	9921
13033	‖	1.1501	1 3 0 1 1 1 1	13039	1032000	*	$4_2\ a\ 0\ 0$	13034
9745	‖	1.166	1 0 2 1 1 1 1	*		*	$2_2\ s\ 1\ 2_0\ a$	9709
11663	‖	1.156	2 0 2 1 1 1 1	*		11667	$2_2\ s\ 2\ 2_0\ a$	11632
12711	‖	1.156	1 2 1 0 2 0 0	*	1030200	12707	$3_3\ a\ 1\ 2_2\ s$	12706
9668	‖	1.1634	1 1 1 0 2 0 0	9614		*	$2_2\ a\ 1\ 2_2\ s$	9350
11570	‖	1.1556	2 1 1 0 2 0 0	11510		*	$2_2\ a\ 2\ 2_2\ s$	11577
14597	‖	1.151	2 2 1 0 2 0 0	*	2030200	14607	$3_3\ a\ 2\ 2_2\ s$	14618
2702	⊥		1 0 0 1 0 1 0	2712		2706	$0\ \ 1\ 1_1\ a$	2691
9366	⊥		1 2 0 1 0 1 0	9343	?		$2_0\ s\ 1\ 1_1\ a$	9363
9085	⊥	1.158	1 1 1 0 1 0 1	9057		9081	$2_2\ a\ 1\ 1_1\ s$	9087
15081	⊥		1 3 1 0 1 0 1	15160	1130101	15162	$4_4\ a\ 1\ 1_1\ s$	15169
18088	⊥		1 4 1 0 1 0 1	18077	1050101	18066	$5_5\ a\ 1\ 1_1\ s$	18072
9177	‖		1 0 2 1 0 1 0	9260		9193	$2_2\ s\ 1\ 1_1\ a$	
9151	‖	1.1524	3 0 1 0 0 0 0	9114		9114	$1_1\ a\ 3\ 0$	9151
11586	‖	1.1584	3 1 0 1 3 1 1	11565		*	$1_1\ s\ 3\ 4_2\ a$	11566
12733	‖	1.1643	3 1 0 1 5 1 1	12731		12734	$1_1\ s\ 3\ 6_4\ a$	12632
2643	⊥		0001010—0 1 0 0 0 0 0	2643			$0\ \ 0\ 1_1\ a$ — $1_1\ s\ 0\ 0$	
716	⊥		0000101—0 0 0 1 1 1 1	716			$0\ \ 0\ 1_1\ s$ — $0\ \ 0\ 2_0\ a$	
2669	⊥		„ —0 0 1 0 0 0 0	2670			„ — $1_1\ a\ 0\ 0$	
2683	⊥		„ —1 0 0 1 1 1 1	2674			„ — $0\ \ 1\ 2_0\ a$	
4077	⊥		„ —0 1 0 1 1 1 1	4068			„ — $1_1\ s\ 0\ 2_0\ a$	
9603	‖	1.1697	„ —0 2 1 0 1 0 1	9601	0030101	9592	„ — $3_3\ a\ 0\ 1_1\ s$	
9802	‖	1.161#	„ —0 0 3 0 1 0 1	9781	0210101	9799	„ — $3_1\ a\ 0\ 1_1\ s$	
12618	‖	1.152	„ —0 3 1 0 1 0 1	12620	0130101	*	„ — $4_4\ a\ 0\ 1_1\ s$	
15521	‖	1.146	„ —0 4 1 0 1 0 1	15539	0050101	*	„ — $5_5\ a\ 0\ 1_1\ s$	

In Table XXIII, the second column gives the observed values of B for the upper vibrational states as given by Funke and Lindholm, except for the few marked by # which are taken from the work of Mecke and Ziegler[6]. In the last column, the calculated frequencies are taken from the papers of Mecke and Ziegler and of Funke and Lindholm. Under the classifications of Wu-Kiang and of modified Herzberg-Spink, the frequencies marked by * are the ones employed for the calculation of the anharmonicity coefficients. They are given below.

	Wu-Kiang	Modified Herzberg & Spink		Wu-Kiang	Modified Herzberg & Spink
ν_1	1984	1987	x_{12}	-3	-5
ν_2	3421	3358	x_{13}	-9	-5
ν_3	3293	3318	x_{14}	10	4
ν_4	$729-x_{44}$	729.5	x_{15}	-25	-17
ν_5	602	603	x_{23}	-147	-112
x_{11}	-11	-13	x_{24}	-9	-9.3
x_{22}	-49	13.6	x_{25}	-11	-10
x_{33}	-5	-28	x_{34}	0	-5
x_{44}	?	-0.5	x_{35}	-18	-16
x_{55}	10	9	x_{45}	-13	-13
			x_{333}		-2.3
			x_{555}		-0.55

Table XXIV. Anharmonicity coefficients of C_2H_2

From Table XXIII, it is seen that so far as agreement between the calculated and the observed frequencies is concerned, the classifications of Mecke-Ziegler and of Wu-Kiang are about equally good, while that of the modified Herzberg-Spink system is somewhat better. One must notice, however, that with this the agreement is poorest in the case of the 6500 and 8450 cm^{-1} bands when it is expected to be good for such simple combination bands. Also it does not seem easy to account for the observed 9906 and 9366 cm^{-1} bands. We should perhaps regard none of these classifications as final, and an analysis of the spectrum of C_2D_2 would be most useful for settling this problem.

With the values (Wu-Kiang) of the coefficients in Table XXIV the zedoth order frequencies can be calculated from (56),

$$\omega_1=2016, \quad \omega_2=3565, \quad \omega_3=3393, \quad \omega_4+3x_{44}=741.5 \quad \omega_5=622 \qquad (57)$$

On neglecting k_4, the constants in the potential (44) can be determined.[14]

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[14] Compare these values with the following obtained with the observed frequencies by Colby, Phys. Rev. 47, 388, (1935),

$$k_{CH}=5.85, \qquad k_{CC}=15.59, \qquad k_3=0.028. \qquad (60)$$

With the modified Herzberg-Spink system, one finds, corresponding to (57) and (58),

$$\omega_1=2017, \quad \omega_2=3422, \quad \omega_3=3425, \quad \omega_4=748.6, \quad \omega_5=620, \qquad (61)$$

and

$$k_{CH}=6.40, \qquad k_{CC}=15.7, \qquad k_3=-0.83. \qquad (62)$$

$$k_{CH} = 6.24\,, \qquad k_{CC} = 17.2\,, \qquad k_3 = -\,0.67 \tag{58}$$

The deformation force constants in the potential (48) can be calculated with the observed frequencies ν_4 and ν_5, since ω_4 is not known but is expected to be not very different from the observed value. Thus Colby obtained

$$k_\alpha = 2.44\,, \qquad k'_\alpha = 0.92 \times 10^{-12}. \tag{59}$$

The constants in the anharmonic potentials have been estimated by Wu[5]. In view of the uncertainties in the classifications of the bands, we shall not give these constants here but refer to the paper.

1a, 1b) C_2HD, C_2D_2

The Raman spectra of these molecules have been studied by Glockler, Davis and Morrell[1]. The infrared spectra have been studied by Randall and Barker in the region of the fundamentals with a prism instrument[2], and the photographic bands of C_2HD have been analyzed by Herzberg, Patat and Verleger[3]. The classification of the fundamental frequencies is guided by the calculations of Colby who obtained the frequencies of these molecules with the potentials (48) and (44) and the constants determined from C_2H_2. The following table summarizes the observed data and their interpretations.

Assignment	C_2HD		C_2D_2	
	Obs.	Calc.	Obs.	Calc.
ν_1	1851 Ra.	1840	1762 Ra.	1750
ν_2	3335 Ra.	3335	2700 Ra.	2690
ν_3	2585 Inf.	2560		2414
ν_4	679 Inf.	669	539 Inf.	535
ν_5	519 Inf.	523		505
$\nu_4+\nu_5$	1202 Inf.	1192	1043 Inf.	1040

Table XXV. Vibrational spectra of C_2HD and C_2D_2

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[1] G. Glockler and H. M. Davis, Phys. Rev. 46, 535, (1934); Glockler and C. E. Morrell, *ibid.*, 47, 569, (1935); Jour. Chem. Phys. 4, 15, (1936).

[2] H. M. Randall and E. F. Barker, Phys. Rev. 45, 124, (1934).

[3] G. Herzberg, F. Patat & H. Verleger, Zeits. f. Physik 102, 1, (1936).

Obs. ν	Assignment	Obs. ν	Assignment	Calc. ν
8409.4 ∥	$\nu_1+2\nu_2$	9706.36 ∥	$3\nu_2$	*
9050.6 ⊥	$\nu_1+2\nu_2+\nu_4$	10211 ⊥	$3\nu_2+\nu_5$	10219
9115.5 ∥	$2\nu_2+\nu_3+\nu_5-\nu_5$	11526 ∥	$\nu_1+3\nu_2$	11539
9138.88 ∥	$2\nu_2+\nu_3$	12263.03 ∥	$3\nu_2+\nu_3$	12266.6
9404.75 ∥	$\nu_1+3\nu_3$	12735.0 ∥	$4\nu_2+\nu_5-\nu_5$	12723
9691.9 ∥	$3\nu_2+\nu_5-\nu_5$	12746.77 ∥	$4\nu_2$	12742.4

Table XXVa. Vibrational spectrum of C_2HD

From the first 7 bands in Table XXVa and the 1202 cm^{-1} band in Table XXV, the following partial determination of the anharmonicity coefficients can be made

$$\begin{aligned} &x_{22}=-49.8 \qquad x_{12}=-6 \qquad x_{23}=-8.2 \qquad x_{25}=-4.9 \\ &x_{35}=-13.8 \qquad x_{45}=4 \qquad 3x_{33}+x_{13}=-67.1 \\ &2x_{24}+x_{14}=-37.8 \end{aligned} \tag{63}$$

The dimensions of the C_2H_2 and C_2HD molecules have been determined from the rotational structures of the observed bands by Herzberg, Patat and Verleger[4], who gave the following values for $B_0=h/8\pi^2I_0$ in equations (81) and (82) of Chap. IV, and $B_e=B_0+\frac{1}{2}(\alpha_1+\alpha_2+\alpha_3)+\alpha_4+\alpha_5$,

$$\begin{aligned} &I_0\,(C_2H_2)=23.492\,, \qquad I_0\,(C_2HD)=27.888\times10^{-40}, \\ &I_e\,(C_2H_2)=23.355\,, \qquad I_e\,(C_2HD)=27.740, \\ &r_0\,(C-H)=1.057\ \text{Å}, \qquad r_0\,(C-C)=1.199\ \text{Å}. \end{aligned} \tag{64}$$

Comparison of the C—H bond distance in C_2H_2 with that in HCN, (18), shows that the higher value 6.24×10^5 for the bond constant (58) is more in line with the Badger[5] relation between bond constant and bond distance than the value 5.85×10^5 obtained with the observed frequencies uncorrected for anharmonicities.

2) C_2N_2

This molecule is known to be linear and symmetrical from electron diffraction measurements[1] which give $r(C-C)=1.37$ Å and $r(C-N)=1.155$ Å. The assignment of the fundamental frequencies has been discussed by a number of authors[2] and most recently by Stevenson[3]. The following table summarizes the various assignments and the potential constants calculated according to (45) and (49).

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[4] The values of the α's are obtained by Herzberg, Patat and Verleger empirically according to their classification of the observed bands. According to the classification of Wu and Kiang, slightly different values for the α's are obtained, but the change in the value of the B would be negligible. The value 6.54×10^{-27} has been employed for the Planck constant *h* in obtaining the values of the *I*'s.

[5] R. M. Badger, Jour. Chem. Phys. 3, 710, (1935).

	Woo-Badger	Kistiakowsky-Gershinowitz	Eucken-Bertram	Woo-Liu-Chu
ν_1	860 Ra.	860	860	756 Ra.
ν_2	2336 Ra.	2336	2336	2336
ν_3	2150 Inf.	2150	2150	2150
ν_4	230 Inf.	512 Ra.	740?	230
ν_5	510 Ra.	756 Ra.	510	510
k_{C-C}	6.7			5.1
k_{CN}	17.5			17.5
k_8	0.58			0.10
k_α	2.9×10^{-12}		15.5×10^{-12}	2.9×10^{-12}
k'_α	-0.24		12.3	-0.24

Table XXVI. Fundamental frequencies & potential constants of C_2N_2

Concerning the symmetrical vibration ν_1, the argument of Woo, Liu and Chu for assuming the Raman frequency 756 is that the C—C bond constant so obtained is in better accord with the values for the same bond in other molecules. Stevenson pointed out recently that this value 5.1 for the C—C constant leads to a carbon-carbon distance 1.41 Å according to Badger's relation, while the value 6.7 obtained with $\nu_1=860$ leads to $r(C-C)=1.35$ Å, in better agreement with the observed value. Both the observed C—C distance and the bond constant 6.7×10^5 suggest some double bond contributions arising from quantum mechanical resonance. It seems that the original assignment of Woo and Badger is more satisfactory on these considerations,[4]

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[1] L. Pauling, H. D. Springall & K. J. Palmer, Jour. Am. Chem. Soc. 61, 927, (1939).

[2] S. C. Woo and R. M. Badger, Phys. Rev. 39, 932, (1932); G. B. Kistiakowsky and H. Gershinowitz, Jour. Chem. Phys. 1, 443, (1933); Woo, T. K. Liu & T. C. Chu, Jour. Chin. Chem. Soc. 3, 301, (1935); Woo, Zeits. f. Phy. Chem. B, 37, 399, (1937); A. Eucken and A. Bertram, *ibid.*, B 31, 361, (1936).

[3] D. P. Stevenson, Jour. Chem. Phys. 7, 171, (1939).

[4] In fact, with the assignment $\nu_1=756$ (whose existence in the Raman spectrum is not entirely without question, see Kohlrausch, *Der Smekal-Raman Effekt*, P. 321), it is not easy to explain the 860 cm^{-1} Raman line and the 622 cm^{-1} infrared band (which can otherwise be explained as the difference band $\nu_1-\nu_4=860-230$ cm^{-1}).

For the deformation vibrations, the assignment of Kistiakowsky and Gershinowitz can be dismissed on consideration of the selection rules. Eucken and Bertram from specific heat measurements suggested that ν_4 might be 740 cm^{-1} and that the 230 cm^{-1} band[5] is a difference band $\nu_4 - \nu_5$. This leads, however, to values for the deformation constants which are too large compared with similar constants in other molecules. It seems that further work on the infrared and the Raman spectra and the specific heats at low temperatures is desirable in order to definitely fix the fundamental frequencies of the molecule and hence the potential function.

B) Pyramidal YX_3 Molecules

Consider a symmetrical pyramidal molecule with 3 identical atoms each of mass *m* at the corners of the base and an atom of mass *M* at the vertex. Of the six degrees of freedom for vibrational motion, there are two parallel vibrations which are symmetrical with respect to the axis of symmetry, and two perpendicular vibrations which are doubly degenerate since the motion of the Y atom is isotropic in directions perpendicular to the symmetry axis. The forms of these vibrations are shown in Fig. 26.

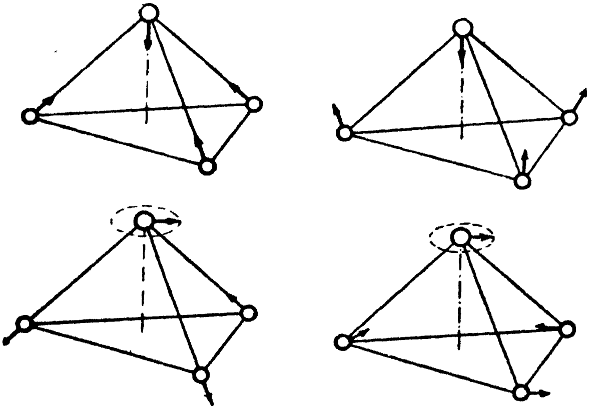

Fig. 26. Normal vibrations of pyramidal YX_3 molecules

The problem of finding the normal frequencies of a pyramidal YX_3 molecule has been worked out for a central force potential by Dennison[1], for a valence force potential by Lechner[2], and for the most general potential consistent with the trigonal axial symmetry by Rosenthal[3].

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[5] J. Strong and S. C. Woo, Phys. Rev. 42, 267, (1932).

[1] D. M. Dennison, Phil. Mag. 1, 195, (1926).

[2] F. Lechner, Wien. Ber. 141, 291, 663, (1932); see also J. B. Howard and E. B. Wilson, Jour. Chem. Phys. 2, 630, (1934).

[3] Jenny E. Rosenthal, Phys. Rev. 47, 235, (1935).

Following Rosenthal, let the normal Y–X distances be denoted by r, their changes by $\delta r_1, \delta r_2, \delta r_3$, the normal X–X distances by q and their changes by $\delta q_{12}, \delta q_{23}, \delta q_{31}$. On introducing the symmetry coordinates x, y, z, t, u, w defined by

$$x+\tfrac{1}{3}u=(q/r)(\delta r_2-\delta r_3), \qquad u=\delta q_{12}-\delta q_{13},$$

$$y+\tfrac{1}{3}t=\frac{2}{\sqrt{3}}(r/q)\left[\tfrac{1}{2}(\delta r_2+\delta r_3)-\delta r_1\right], \quad t=\frac{2}{\sqrt{3}}\left[\tfrac{1}{2}(\delta q_{12}+\delta q_{13})-\delta q_{23}\right], \tag{65}$$

$$3gz+\frac{1}{\sqrt{3}}w=(r/q)(\delta r_1+\delta r_2+\delta r_3), \qquad w=\frac{1}{\sqrt{3}}(\delta q_{12}+\delta q_{23}+\delta q_{31}),$$

where

$$g=h/q=\frac{1}{\sqrt{3}}\cot\beta\,, \tag{66}$$

h being the normal height of the pyramid and β the angle between the Y–X bond and the symmetry axis, the kinetic energy becomes

$$2T=\frac{3\mu}{b}(\dot{x}^2+\dot{y}^2)+3\mu\,\dot{z}^2+\tfrac{1}{3}m\,(\dot{u}^2+\dot{t}^2+\dot{w}^2), \tag{67}$$

where

$$\mu=mM/(M+3m), \qquad b=1+6Mg^2/(M+3m). \tag{68}$$

The most general quadratic potential function is

$$2V=A(x^2+y^2)+Bz^2+Cw^2+D(t^2+u^2)+2E(xu+yt)+2Fzw. \tag{69}$$

The determinantal equation gives for the two || vibrations

$$\begin{aligned}\lambda_1+\lambda_3&=\frac{1}{3\mu}B+\frac{3C}{m}\,,\\ \lambda_1\cdot\lambda_3&=\frac{1}{m\mu}(BC-F^2)\,,\end{aligned} \tag{70a}$$

and for the two ⊥ vibrations

$$\begin{aligned}\lambda_2+\lambda_4&=\frac{b}{3\mu}A+\frac{1}{m}3\,D,\\ \lambda_2\cdot\lambda_4&=\frac{b}{m\mu}(AD-E^2)\end{aligned} \tag{70b}$$

It is seen that in general, the four distinct frequencies are not sufficient for the evaluation of the six constants in (69).

If instead of the general potential (69) one expresses it as the sum of valence and central force potentials

$$2V = \sum_{i \neq j} \left(\frac{\partial V}{\partial q} \right)_0 \delta q_{ij} + 2\sum_i \left(\frac{\partial V}{\partial r} \right)_0 \delta r_i + \sum_i \left(\frac{\partial^2 V}{\partial r^2} \right)_0 (\delta r_i)^2 + \tfrac{1}{2}\sum \left(\frac{\partial^2 V}{\partial q^2} \right) (\delta q_{ij})^2$$

$$+ \tfrac{1}{2} k_\alpha \sum_{i \neq j} (r\,\delta\alpha_{ij})^2 + k'_\alpha (\tfrac{1}{3}\, r\,\delta S)^2, \qquad (71)$$

where $\delta\alpha_{ij}$ is the change of the angle α between the $Y-X_i$ and $Y-X_j$ bonds and $2S$ is the trihedral angle at the top of the pyramid, then for equilibrium, one has

$$\left(\frac{\partial V}{\partial q} \right)_0 = \left(\frac{\partial V}{\partial r} \right)_0 = 0 .$$

On writing

$$\left(\frac{\partial^2 V}{\partial r^2} \right)_0 = k , \qquad \left(\frac{\partial^2 V}{\partial q^2} \right)_0 = k_1 , \qquad (72)$$

the following relations result:

$$\begin{aligned} A &= \tfrac{8}{2}(f + 3f_4), & B &= 3[3g^2 f + f_2 + 36 g^2 f_4], \\ C &= \tfrac{1}{3} f + g^2 f_2 + f_1 + 36 g^4 f_4, & & \\ D &= \tfrac{1}{6} f + \tfrac{1}{2} f_1 + \tfrac{1}{2}(1+6g^2)^2 f_4, & E &= \tfrac{1}{2} f - \tfrac{8}{2}(1 + 6g^2) f_4, \qquad (73) \\ F &= \sqrt{3}\, g\, (f - f_2 - 36 g^2 f_4), & & \end{aligned}$$

where

$$f = k/(1 + 3g^2), \quad f_1 = k_1, \quad f_2 = k'_\alpha / (1 + 12g^2),$$

$$f_4 = k_\alpha / (1 + 3g^2)(1 + 12g^2).$$

In this case, the number of independent constants is 4, there being two relations among the six constants A, B, ... F from (73),

$$A(1 + 6g^2) + 3E - B - \sqrt{3}\, F/g = 0,$$

$$3(2D - C) + 2E(1 + 6g^2) - F(1 + 3g^2)/\sqrt{3}\, g - \tfrac{1}{2} B = 0. \qquad (74)$$

These two relations form a criterion as to how well the molecule can be described by the less general potential (71).

If in (71) one makes the further simplification that $k_\alpha = k'_\alpha = 0$, then equations (70) reduce to the expressions obtained by Dennison for the central force potential, namely,

$$\lambda_1 + \lambda_3 = \frac{k}{m}\left(1 + \frac{3m}{M}\cos^2\beta\right) + \frac{3}{m} k_1$$

$$\lambda_1 \cdot \lambda_3 = \frac{3}{m\mu} \cos^2\beta\, k\, k_1 \qquad (75a)$$

$$\begin{aligned}\lambda_2+\lambda_4&=\frac{k}{2m}\left(2+\frac{3m}{M}\sin^2\beta\right)+\frac{3}{2m}\,k_1\\ \lambda_2\cdot\lambda_4&=\frac{3}{4m\mu}\left(1+\frac{M-3m}{M+3m}\cos^2\beta\right)k\,k_1.\end{aligned}\tag{75b}$$

If in (71) one puts $k_1=k_\alpha=0$, equations (70) reduce to those obtained by Lechner for the simple valence force potential,

$$\begin{aligned}\lambda_1+\lambda_3&=\frac{k}{m}\left(1+\frac{3m}{M}\cos^2\beta\right)+\frac{12k_\alpha}{m}\,\frac{\cos^2\beta}{1+3\cos^2\beta}\left(1+\frac{3m}{M}\sin^2\beta\right)\\ \lambda_1\cdot\lambda_3&=\frac{12\,k\,k_\alpha}{m\mu}\,\frac{\cos^2\beta}{1+3\cos^2\beta}\end{aligned}\tag{76a}$$

$$\begin{aligned}\lambda_2+\lambda_4&=\frac{k}{2m}\left(2+\frac{3m}{M}\sin^2\beta\right)+\frac{3k_\alpha}{m(1+3\cos^2\beta)}\left(1+\cos^2\beta+\frac{3m}{2M}\sin^4\beta\right)\\ \lambda_2\cdot\lambda_4&=\frac{3\,k\,k_\alpha}{m^2(1+3\cos^2\beta)}\left(1+\cos^2\beta+\frac{3m}{M}\sin^2\beta\right).\end{aligned}\tag{76b}$$

As there are only two independent constants in either the central force or the valence force potential, equations (75) and (76) will in general not be compatible with the four observed frequencies, unless the molecule in question happens to be capable of accurate description by a central or valence force potential. Hence in the next approximation, one tries to include some cross terms in the potential. But as there is no unique way of doing this, there are always some arbitrariness and ambiguity inherent in potentials other than that demanded by the symmetry of the molecule. For practical purposes, however, some less general potentials suggested by empirical knowledge are usually sufficiently accurate. An example of this is the following modified valence potential

$$\begin{aligned}2V=k\,\Sigma\,(\delta r_i)^2+k_\alpha\,\Sigma\,(r\delta\alpha_i)^2+2k'\,(\delta r_1\,\delta r_2+\delta r_2\,\delta r_3+\delta r_3\,\delta r_1)+\\ 2k_\alpha''\,r^2\,(\delta\alpha_1\,\delta\alpha_2+\delta\alpha_2\,\delta\alpha_3+\delta\alpha_3\,\delta\alpha_1).\end{aligned}\tag{77}$$

For this potential, the frequencies can be obtained from (76) by replacing k and k_α in (76a) by $k+2k'$ and $k_\alpha'+2k_\alpha''$, and in (76b) by $k-k'$ and $k_\alpha-k_\alpha''$ respectively.

1) NH_3

The infrared and the photographic regions of the spectrum of NH_3 have been the subject of many extensive and detailed investigations[1-3]. The Raman spectrum of the gas has also been studied by a number of workers.[4] We shall discuss the results for this molecule in some details because it shows the kind of quantum mechanical effect of penetration through a potential barrier discussed in §4, A, 1) of Chap. III.

That the molecule has a pyramidal structure is now established on electric moment (1.44×10^{-18} e.s.u.) and spectroscopic data. The high resolution work of Stinchcomb and Barker shows that there are two types of vibration-rotational bands: the two intense bands at 950 and 3337 cm^{-1} are of the parallel type and the other intense band at 1630 cm^{-1} is of the perpendicular type, discussed in §2, Chap. IV. These have been assigned as the fundamentals ν_1, ν_3, ν_4 of Fig. 26. There has been considerable uncertainty as to the location of the fourth fundamental. Recently, from a study of two $\perp$ type bands at 2457 and 4420 cm^{-1}, Barker[5] came to the conclusion that they are to be explained as the combination bands $\nu_2-\nu_3$ and $\nu_2+\nu_3$ respectively. This places the fundamental ν_2 at 3415 cm^{-1}. That this has not been found earlier is due to its being overlapped by the strong parallel fundamental $\nu_1=3337$, as already observed by Hardy.[6] It is now quite certain that the four fundamentals are as given in Table XXVII.

The Raman spectrum of the NH_3 gas shows 3 strong lines at 3335, 933 and 967 cm^{-1}. The non-appearance of the two $\perp$ vibrations is probably due to their low intensities expected of degenerate vibrations in general. The weak line at 1922 cm^{-1} observed by Amaldi and Plazcek and that at 3219 cm^{-1} observed by Lewis and Houston can be explained as $2\nu_3$ and $2\nu_4$ respectively. The assignment of the latter frequency is supported by the observation of a band at 3219 cm^{-1} in the

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[1] Near infrared: G. A. Stinchcomb & E. F. Barker, Phys. Rev. 33, 305, (1929); Barker, *ibid.*, 33, 684, (1929); D. M. Dennison & J. D. Hardy, *ibid.*, 39, 938, (1932); H. J. Unger, *ibid.*, 43, 123, (1933).

[2] Photographic region: R. M. Badger & R. Mecke, Zeits. f. phys. Chem. B 5, 333, (1929); Badger, Phys. Rev. 35, 1038, (1930); P. Lueg and K. Hedfeld, Zeits. f. Physik 75, 599, (1932); S. H. Chao, Phys. Rev. 50, 27, (1936).

[3] Far infrared: R. M. Badger & C. H. Cartwright, Phys. Rev. 33, 692, (1929); N. Wright & H. M. Randall, *ibid.*, 44, 391, (1933); R. B. Barnes, *ibid.*, 47, 658, (1935).

[4] For earlier work, see Kohlrausch, *Der Smekal-Raman Effekt*. E. Amaldi and G. Placzek, Zeits. f. Physik 81, 259, (1933); C. M. Lewis and W. V. Houston, Phys. Rev. 44, 903, (1933).

[5] E. F. Barker, Phys. Rev. 55, 657, (1939); 52, 250, (1937).

[6] J. D. Hardy, Phys. Rev. 40, 1039, (1932); also Dennison and Hardy, *ibid.*, 39, 938, (1932).

infrared by Barker.[5] The very weak lines at 2270 and 2210 cm^{-1} found by Amaldi and Placzek cannot be readily accounted for; but as they have not been found by Lewis and Houston, it is not entirely beyond doubt that they are genuine NH_3 lines.

The results of the various authors on the infrared and the Raman and photographic bands are summarized in Table XXVII.

Assignment	Observed freq.			$\Delta\nu_\parallel$	$\Delta\nu_\perp$	
	Raman	Infrared			obs.	calc.
ν_1	3334	3337	$\parallel$	19.88		
ν_3	934.0	933	$\parallel$	19.88		
	964.2	967	$\parallel$	19.88		
ν_2		(3415)	$\perp$		(16)	7.15
ν_4		1628	$\perp$		3-4	5.75
$2\nu_3$	1922	1910	$\parallel$			
$\nu_2-\nu_3$		2440.8	$\perp$		16	
		2473.3	$\perp$		16	
$3\nu_3$		2860	$\parallel$			
$2\nu_4$	3219	3219	$\parallel$			
$2\nu_4+\nu_3$		4177	$\parallel$			
		4217	$\parallel$			
$\nu_1+\nu_3$		4270	$\parallel$			
		4303	$\parallel$			
$\nu_2+\nu_3$		4434	$\perp$		16	
		4506	$\perp$		16	
$\nu_2+\nu_4$		5055	$\perp$		9.98	9.94
$\nu_2+\nu_4+\nu_3$		6020			10.2	
$2\nu_1$		6599	$\parallel$	19.7		
		6627	$\parallel$	19.8		
$2\nu_2+\nu_3$		7670				
$2\nu_1+\nu_4$?		8175	$\parallel$	21.3		
		8202	$\parallel$	20.8		
$2\nu_2+\nu_4$		8460			11.3	
$3\nu_1$		9760.4	$\parallel$			
$\nu_1+2\nu_2$		10099.7	$\parallel$			
		10104	?			
		11215				
$4\nu_1$, $2\nu_1+2\nu_2$, etc.		12609.7	$\parallel$			
		12619.7	$\parallel$			
		15540	?			
		18200	?			

Table XXVII. Vibrational spectrum of NH_3

A striking feature in the spectrum of NH_3 is that the 950 cm^{-1} band really consists of two $\parallel$ type bands with their *Q* branches at 933 and 967 cm^{-1}. With a spectrometer of still higher resolving power, Dennison and Hardy showed that the 3337 cm^{-1} band also consists of two $\parallel$ type bands separated by about 1.6 cm^{-1}. These doublings of the fundamentals are explained as the result of the splitting of the energy levels as discussed in §4, A, 1), Chap. III. That the two fundamentals show different separations of *ca.* 1.6 and 34 cm^{-1} can be understood in a qualitative manner as follows: In the vibration ν_1, the distances between the H atoms decrease as the N atom approaches the plane of the H atoms, while in ν_3, the H atoms spread further apart as the N atom approaches their plane, as shown in Fig. 26. Consequently, the rise of the potential when the N atom approaches the plane of the H atoms is higher in the vibration ν_1 than in ν_3. As shown in Chap. III, §4, A, 1), the splitting of the energy level is accordingly greater in ν_3 than in ν_1.

This explanation of the doubling of the || bands, first given by Hund in a qualitative manner,[7] is supported by the following evidences:

(i) It is possible to calculate the intensities of the rotational lines in the ν_1 and ν_3 bands in the manner indicated in Chap. IV, §2, taking into consideration the symmetry properties of the energy levels shown in Fig. 13, and the modification in the statistical weights of the rotational levels due to the inclusion of the nuclear spins of the three H atoms. Dennison and Hardy[1] found that the calculated intensities of both component bands in ν_1 and ν_3 are in complete agreement with their own observations and those of Stinchcomb and Barker.[1]

(ii) For the same reason as given in Chap. III, §4, A, 1), the permanent electric moment of the molecule has a non-vanishing matrix element only between the symmetrical and the antisymmetrical levels O_s and O_a of the normal vibrational state. Hence the rotational lines in the pure rotational spectrum arise from transitions between the rotational levels associated with the level O_s and those with O_a. As a result, each rotational line should be double, with a separation equal to $2\Delta_0$. As the splitting Δ_0 is small compared with kT, the relative intensities of the two components of each line will not depend greatly on the Boltzmann factor but largely on the statistical weights of the levels involved. By means of a grating spectrometer of large aperture and high resolving power, Wright and Randall[8] succeeded in resolving the doublets of the rotational lines $J=5$, 6, 7 in the pure rotational spectrum. The doublet separation observed is 1.33 cm^{-1}. This gives the splitting for the normal state

$$\Delta_0 = 0.67\ \mathrm{cm}^{-1}, \tag{78}$$

The observed intensities are found to be also in good agreement with the theoretical values.

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[7] F. Hund, Zeits. f. Physik 43, 805, (1927).

(iii) Direct transition from the symmetrical level O_s to the antisymmetrical level O_a has been observed by Cleeton and William[8] who studied the absorption by NH_3 gas of ultrashort electromagnetic waves (1 to 4 cm wave length) generated by specially constructed magnetrons. The absorption maximum was located by means of a large echelette grating at $\lambda=1.25$ cm. When correction for the asymmetry of the absorption line is made, the agreement with the expected position $\lambda=1/0.67=1.5$ cm is good.

(iv) On assuming the potential $V(x)$ in Fig. 12 to be two parabolas joined by a horizontal line, Dennison and Uhlenbeck have calculated the height of the pyramid h and the height of the potential barrier from the observed splittings of the normal state and the state $v_3=1$.[9] The result is

$$h = 0.388 \text{ Å} \qquad (79)$$

On combining this with the moment of inertia I about an axis perpendicular to the symmetry axis obtained by Wright and Randall from the pure rotational spectrum, namely, from the expression

$$\begin{aligned} \nu &= 19.880\,J - 0.00176\,J^3, \\ I_A &= 2.782\times 10^{-40}\,\text{g.cm}^2, \end{aligned} \qquad (80)$$

one obtains the following dimensions

$$r(\text{N}-\text{H}) = 1.01 \text{ Å}, \qquad r(\text{H}-\text{H}) = 1.61 \text{ Å} \qquad (81)$$

The agreement between these values and those obtained from the values of I_A for NH_3 and ND_3 (see ND_3) lends further support to the theory of the doubling.

We shall now consider the harmonic and combination bands in the infrared and the photographic region (Table XXVII). Symmetry considerations similar to those given in §3, Chap. IV, require that one must distinquish 4 classes of wave functions, namely, the α and β classes which are symmetrical and antisymmetrical respectively with respect to the interchange of two H nuclei, and the γ and δ classes which are symmetrical and antisymmetrical respectively with respect to the interchange of a certain pair of the H nuclei, say 1 and 2, but are neither symmetrical nor antisymmetrical with respect to the other pairs, 1 and 3, or 2 and 3.[10] Corresponding to the double degeneracy, states with the γ and δ wave functions always have the same energy. The wave functions of states with v_1 and v_3 arbitrary and $v_2=v_4=0$ belong to the α and β classes, while those of states with $v_2\neq 0$, $v_4\neq 0$ can be shown to consist of a number of wave functions of the α β, (γ, δ) classes. Each of these corresponds to a different energy when the effects of resonance doubling and of anharmonicity of the vibrations are taken into account. The structure of the band (*i.e.*, whether the change of the electric moment is $\|$ or $\perp$ to the symmetry axis) is closely connected with the symmetry properties of the wave functions of the two states involved in the transition in question. It can be shown that the fundamentals ν_1 and ν_3 and their harmonics or combinations are of the $\|$ type; and the fundamentals ν_2 and ν_4 consist of one $\perp$ type band each; their first harmonic $2\nu_2$ or $2\nu_4$ consists of one $\|$ and one $\perp$ type band; the combination $\nu_2+\nu_4$ of one $\perp$ and two $\|$ type bands; the second harmonic $3\nu_2$ or $3\nu_4$ also of one $\perp$ and two $\|$ type bands. The separations between the component bands depend on the anharmonicity of the vibrations. When the separations are small, a high harmonic or combination band involving the $\perp$ vibrations would consist of a number of bands overlapping one another. This renders the analysis of the rotational structure exceedingly difficult.

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[8] C. E. Cleeton and N. H. William, Phys. Rev. 45, 234, (1934).

[9] The value h given here is that obtained by Wright and Randall with the formula of Dennison and Uhlenbeck, Phys. Rev. 41, 313, (1932), and the value $\Delta_0=0.67$ cm^{-1},which is considered more accurate than the value $\Delta_0=0.80$ obtained by Dennison and Hardy from the 3337 cm^{-1} band. M. F. Manning, Jour. Chem. Phys. 3, 136, (1935), employed a more smooth potential curve than the flat-top one of Dennison-Uhlenbeck, for which the Schrödinger equation can be solved exactly. The calculated positions of the ν_3 bands of NH_3 and ND_3 are found to be in good agreement with the observed positions.

In NH_3, the situation is further complicated by the close proximity of the frequencies of ν_1 and ν_2. Thus for example, the region at $\sim$10000 cm^{-1} may contain all the bands due to $3\nu_1$, $2\nu_1+\nu_2$, $\nu_1+2\nu_2$, and $3\nu_2$, a total of 4 parallel and 3 perpendicular type bands. For this reason, the analysis of the photographic bands at 10,230 Å, 8800 Å, 7920 Å, 6470 Å and 5490 Å by Lueg and Hedfeld, and by Badger and Mecke[2] can only be regarded as partial. The more recent and detailed analysis of Chao[2] of these regions shows that the rotational structures are exceedingly complicated. By an application of the method of second differences familiar in the analysis of the spectra of diatomic molecules, Chao succeeded in identifying a few bands of the parallel type, whose centers are given in Table XXVII. The high complexity, however, of the spectrum defies his effort to analyze the observed lines into the theoretically expected number of component bands. Until a complete analysis is available, any assignment such as given in Table XXVII must be regarded as tentative.

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[10] For details of these symmetry considerations, see D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

[11] M. Johnston and D. M. Dennison, Phys. Rev. 48, 868, (1935).

Finally, we must mention another interesting feature in the observed spectrum of NH_3, namely, the anomaly in the separation of the Q branches in the $\perp$ type bands that have been resolved (Table XXVII). The explanation is the interaction between vibration and rotation of the type briefly discussed in §4, Chap. IV. Johnston and Dennison[11] have calculated the internal angular momenta $\xi(h/2\pi)$ of these vibrations and from them the theoretical separations $\Delta\nu$. It is seen that the agreement between the calculated and the observed values of $\Delta\nu$ is not satisfactory except in the 5055 cm^{-1} band.

1a) ND_3, 1b) NH_2D, 1c) NHD_2

The infrared absorption spectrum of ND_3 has been studied by Migeotte and Barker[1] under high dispersion, and the Raman spectrum by Wall and Glockler.[2] Two parallel type bands are found at 2420 and 750 cm^{-1}, the latter being double with their centers at 745.5 and 749.2 cm^{-1} and corresponding to the 950 cm^{-1} band of NH_3. The experimental data on ND_3 and the other molecules NH_2D and NHD_2, for which only the Q branches of the low frequency parallel fundamental ν_3 are known, are summarized in Table XXVIII and Table XXIX.

Vibration	Obs. ν &	type	$\Delta\nu$ cm^{-1} Obs.	calc.
ν_1	2420	$\parallel$	10.22	
	2420	Ra.		
ν_3	745.8	$\parallel$	10.22	
	749.2	$\parallel$		
ν_2	2556	$\perp$	1.7	2.7
ν_4	1191.3	$\perp$	3.2	4.8

Table XXVIII. Fundamental frequencies of ND_3

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[1] M. Migeotte and E. F. Barker, Phys. Rev. 50, 418, (1936). This work supercedes the earlier work of S. Silverman and J. A. Anderson, *ibid.*, 44, 1032, (1933), who gave $\nu_3 = 770$ cm^{-1}.

[2] F. T. Wall and G. Glockler, Jour. Phys. Chem. 41, 143, (1937).

NH_3	933	967	34
NH_2D	874	894	20
NHD_2	808	818	10
ND_3	745	748.5	3.5

Table XXIX. Doublings in ν_3 bands
The frequencies given are for the *Q* branches.

It is seen from Table XXIX that the doublet separations in the ν_3 fundamentals of the deutero-ammonias decrease as the number of deuterium atoms increases. This can be understood qualitatively when one remembers that in the vibration ν_3, the hydrogen atoms spread out as the N atom approaches the plane of the H atoms and that with the D atoms replacing the H atoms, the spreading is less and consequently the rise of the potential in Fig. 12 is higher than in NH_3.

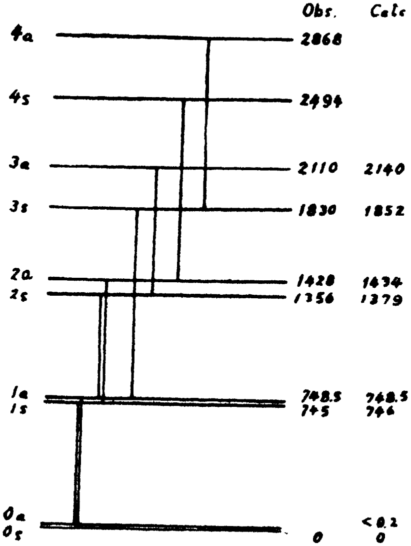

Fig. 27. Vibrational levels of ν_3 in ND_3

Migeotte and Barker observed in the 745 cm^{-1} region of ND_3 a number of weak lines which they ascribed to the *Q* branches of the absorption bands by molecules in the excited states of the vibration ν_3. The observed *Q* branches and their assignments are shown in Fig. 27. It is to be noted that the vibrational levels defined by this scheme are in good agreement with the values calculated by Manning[3] by employing a potential $V(x)$ in Fig. 12 that contains three adjustable parameters. The calculated positions are also given in Fig. 27.

The moment of inertia of ND_3 about an axis $\perp$ to the symmetry axis can be calculated from the line spacing $\Delta\nu = 10.22$ cm^{-1} in the $||$ type fundamentals. Barnes[4] from the measurements on the pure rotational lines $J=8$ to $J=20$ found that these lines can be represented by

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[3] M. F. Manning, Jour. Chem. Phys. 3, 136, (1935).
[4] R. B. Barnes, Phys. Rev. 47, 658, (1935).

$$\nu = 10.26\ J - 0.00045\,J^3.$$

These lead to the value

$$I_A = 5.397 \times 10^{-40}\,\text{g.cm}^2 \tag{82}$$

The dimensions of the NH_3 and ND_3 molecules, on the assumption that they are the same, can be calculated from (80) and (82),

$$h = 0.36\ \text{Å}, \qquad r\,(\text{N}-\text{H}) = 1.016\ \text{Å}. \tag{83}$$

These are in reasonably good agreement with those in (79) and (81).

In Table XXVIII, the observed separations of the Q branches in the $\perp$ fundamentals are given together with the values calculated by Johnston and Dennison.[5]

With the eight observed fundamental frequencies of NH_3 and ND_3, it is possible to determine the six constants in the most general potential (69). The values that are consistent with the 8 frequencies are as follows:

$$\begin{aligned} A &= 10.8, & B &= 6.57, & C &= 1.47, \\ D &= 1.17, & E &= \pm 2.19, & F &= \pm 2.59 \times 10^5. \end{aligned} \tag{84}$$

These values are only approximate since in their calculation the observed rather than the zeroth-order frequencies have been used. To see how well the NH_3 molecule can be described by the less general potential (71), the values in (84) can be substituted into (74). It is found that these relations are not very well satisfied. For this reason, one would hardly expect the simple valence force potential containing only two constants to be sufficiently good.[6]

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[5] M. Johnston & D. M. Dennison, Phys. Rev. 48, 868, (1935), obtained the following values for the constants: $A=9.42$, $D=1.37$, $E=\pm 2.30$.

[6] This is seen from the rather poor agreement between the observed and the calculated frequencies by means of (76a) and (76b) with $k=6.35$, $k_\alpha=0.59$:

NH_3	obs.	$\nu_1=3337$,	$\nu_3=950$,	$\nu_2=3415$,	$\nu_4=1628$,
	calc.	*	1110,	3450,	*

See J. B. Howard, Jour. Chem. Phys. 3, 207, (1935).

2) PH_3, 3) AsH_3

The near infrared spectra of these molecules have been examined under low dispersion by Robertson and Fox.[1] The strong bands of PH_3 at 990, 1121 and 2327 cm^{-1} have been studied under high resolution by Fung and Barker.[2] The Raman spectrum of liquid PH_3 gives three lines at these positions.[4] The pure rotational spectrum of PH_3 was studied by Wright and Randall[3] and no doubling of the lines as in NH_3 was observed. The AsH_3 band at 6138 cm^{-1} was barely resolved into rotational lines by Norris and Unger.[5] These results are summarized in Table XXX.

PH_3				AsH_3			
Assignment	ν Obs.		$\Delta\nu$ Obs.	Assignment	ν Obs.		$\Delta\nu$ Obs.
ν_1	2327	$\parallel$	8.7	ν_1	2122	$\parallel$	
	2306	Ra.					
ν_3	990	$\parallel$	8.5	ν_3	906	$\parallel$	8.5–10
	979	Ra.					
ν_2	992.4	$\perp$	11	ν_2	?		
ν_4	1121.5	$\perp$	11	ν_4	1005		
	1115	Ra.					
$\nu_1+\nu_4$	3428	$\perp$		$\nu_1+\nu_4$	3091		
$\nu_1+2\nu_4$	4541			$2\nu_1$?	4160		
				$3\nu_1$?	6138	$\parallel$	8.187

Table XXX. Vibrational spectra of PH_3 and AsH_3

The absence of doubling of the $\parallel$ type bands in these molecules is probably due to the circumstance that the height of the potential barrier is considerably higher in these molecules than in NH_3. The moment of inertia of PH_3 about an axis $\perp$ to the symmetry axis is accurately known from the pure rotational spectrum to be

$$I_A = 6.22 \times 10^{-40}\ \text{g.cm}^2. \tag{85}$$

For AsH_3, the moment of inertia I_A from the 6138 cm^{-1} band is *ca.* 6.75×10^{-40} g.cm.^{2}

The angle between two P–H bonds is not known directly; but from the absence of the intensification of every third line in the vibration-rotational bands which is expected on account of the nuclear spins of the H atoms, Fung and Barker inferred that the molecule is like a spherical top. This leads to a value $\alpha = 88\frac{1}{2}°$. By analogy with the trihalides of P and As, Yost and Anderson suggested that the angle is about 100°.

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[1] R. Robertson & J. J. Fox, Proc. Roy. Soc. A 120, 161, (1928).
[2] L. W. Fung & E. F. Barker, Phys. Rev. 45, 238, (1934).
[3] N. Wright & H. M. Randall, *ibid.*, 44, 391, (1933).
[4] D. M. Yost & T. F. Anderson, Jour. Chem. Phys. 2, 624, (1934).
[5] W. V. Norris & H. J. Unger, Phys. Rev. 45, 68, (1934).

4) NF_3, 5) PF_3, 6) PCl_3, 7) PBr_3, 8) AsF_3, 9) $AsCl_3$, 10) $SbCl_3$, 11) $BiCl_3$

The Raman spectra of all these trihalides except NF_3 have been studied[1] and the infrared spectrum of NF_3 has been recently reported[2]. That these molecules have pyramidal structures are established on the following evidences: (*i*) the presence of four Raman lines, two completely depolarized and two having low values of the degree of depolarization, are in agreement with the selection rules for a pyramidal model, and (*ii*) electron diffraction measurements show that these molecules have pyramidal structures, the angle between two Y−X bonds being of the order of 100°.[3] The results on these molecules are summarized in Table XXXI.

	ν_1 ∥	ν_2 ⊥	ν_3 ∥	ν_4 ⊥	α
NF_3	908 Inf.	1004 Inf.	505 Inf.	420 Inf.	~110°
PF_3	890	840	531	486	104°
PCl_3	510(0.14)	480 (6/7)	257 (0.29)	190 (6/7)	101°
PBr_3	380(0.28)	400 (6/7)	162 (0.18)	116 (6/7)	~104°
AsF_3	707	644	341	274	(100°)
$AsCl_3$	410(0.08)	370 (6/7)	193 (0.61)	159 (6/7)	103°
$SbCl_3$	338	312	171	147	~ 95°
$BiCl_3$	288	242	130	96	~ 95°

Table XXXI. Fundamental frequencies of trihalides of P, As, Sb, Bi Numbers in parentheses are the degrees of depolarization.

From the four fundamental frequencies in each molecule, Howard and Wilson[4] have calculated the constants in the modified valence potential (77) (except for NF_3). The results are given in Table XXXII.

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[1] Raman spectra: PF_3, D. M. Yost & T. F. Anderson, Jour. Chem. Phys. 2, 624, (1934); 3, 754, (1935); PCl_3, PBr_3, $AsCl_3$, J. Cabannes and Rousset, Ann d. Physique 19, 229, (1933), depolarization; AsF_3, Yost and J. E. Sherborne, Jour. Chem. Phys. 2, 125, (1934); $SbCl_3$, J. Gupta, Sci. and Culture 3, 245, (1937); $BiCl_3$, S. Bhagavantam, Ind. Jour. Phys. 5, 66, 86, (1930).

[2] Infrared spectrum of NF_3, Bailey, Hale & Thompson, Jour. Chem. Phys. 5, 274, (1937).

[3] Electron diffractions by PCl_3, PBr_3, $AsCl_3$, Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

	k	k_α	k'	k''_α
NF_3	3.94	0.65	0.62	0.19
PF_3	4.56	1.07	0.39	0.04
PCl_3	2.11	0.31	0.28	0.06
PBr_3	1.62	0.27	0.15	0.07
AsF_3	3.90	0.40	0.34	0.06
$AsCl_3$	2.01	0.23	0.19	0.02
$SbCl_3$	1.75	0.17	0.16	0.02
$BiCl_3$	1.17	0.10	0.15	0.02

Table XXXII. Potential constants of trihalides of N, P, As and Sb in 10^5 dynes/cm.

12, 13, 14) ClO_3^-, BrO_3^-, IO_3^- ions

The infrared spectra of crystals containing these ions have been studied by Schaefer, Laski[1] and recently by Parodi[2]. The Raman spectra of these ions in crystals and in solutions have been studied by a number of authors[3]. From their apparant similarity with the spectra of the carbonate $CO_3^{=}$ and nitrate NO_3^- ions, it was thought by some writers that these ions have coplanar structures like the latter ions[4]. It was shown by Zachariasen on semi-theoretical ground and by Slater on quantum-mechanical considerations, however, that these ions should have pyramidal structures[5]. Recently, Shen, Yao and Wu have shown, by measurements of the degrees of depolarization of the Raman lines of these ions, that the 982 cm^{-1} line of ClO_3 and the 800 cm^{-1} line of IO_3 are each in reality composed of one intense and one weak lines in close proximity with each other. The presence of four Raman lines, of which two are depolarized and two have low values for the degrees of depolarization, establishes the pyramidal model according to the selection rules. This conclusion is further confirmed by the observation by Parodi of the low frequency vibrations in the infrared. The Raman and the infrared data are summarized in Table XXXIII.[7]

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[4] J. B. Howard and E. B. Wilson, Jour. Chem. Phys. 2, 630, (1934).

[1] Cf. Cl. Schaefer and F. Matossi, *Das Ultrarote Spektrum,* P. 328.

[2] M. Parodi, C. R. 205, 607, (1937).

[3] Cf. K. W. F. Kohlrausch, *Der Smekal-Raman Effekt.*

[4] Schaefer, Matossi & Aderhold, Zeits. f. Physik 65, 289, (1930); R. Titeica, *Spectres d'Vibration et Structure des Molécules Polyatomique,* Paris, 1936.

[5] W. H. Zachariasen, J. Am. Chem. Soc. 53, 2171, (1931); J. C. Slater, Phys. Rev. 38, 325, (1931); R. S. Mulliken, *ibid.*, 40, 55, (1932).

[6] S. T. Shen, Y. T. Yao & T. Y. Wu, Phys. Rev. 51, 235, (1937).

	ν_1 ∥		ν_2 ⊥		ν_3 ∥		ν_4 ⊥	
	Raman	Infra.	Raman	Infra.	Raman	Infra.	Raman	Infra.
ClO_3^-	930 (0.35)	950	982 (6/7)	994	610 (0.56)	624	479 (6/7)	434
BrO_3^-	806 (0.38)	800	836	820	421	434	356 (6/7)	344
IO_3^-	779 (0.43)	780	826 (0.67)	793	390	357	330 (6/7)	322

Table XXXIII. Infrared & Raman spectra of ClO_3^-, BrO_3^-, IO_3^- ions
Numbers in parentheses are the degrees of depolarization.

Since the accuracy of all these frequencies, especially those obtained by the Reststrahlen technique, is very low, it would be meaningless to attempt any refined calculation of the potential functions for these ions. Shen, Yao and Wu have given the constants in the simple valence force potential (76).

	k	k_α	β
ClO_3	5.55	1.07	54°
BrO_3	5.25	0.59	53.5°
IO_3	5.35	0.33	53.5°

Table XXXIV. Potential constants in 10^5 dy./cm.

The regularity in the values of the angle β and the constants k and k_α so obtained is quite marked. These constants, however, must not be regarded as more than giving the order of magnitudes; for in molecules as these, the potential can hardly be expected to be the simple valence force type assumed in the calculation.

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[7] Recently, Th. G. Kujumzelis, Zeits. f. Physik 109, 586; 110, 760, (1938), studied the Raman spectra of these ions and obtained results in complete agreement with those of Shen, Yao, and Wu.

C) Plane Symmetrical YX_3 Molecules

For plane symmetrical molecules, the potential (69) still holds except that now $F=0$, since the potential must be an even function of z, the displacement of the Y atom perpendicular to the plane of the molecule. The normal frequencies are given by (70) with $F=0$. The forms of the vibrations are shown in Fig. 28.[1]

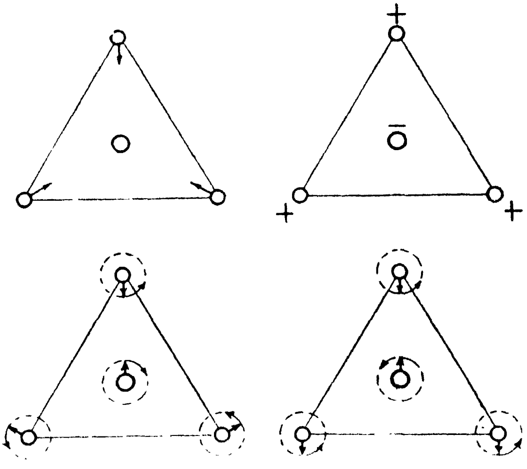

Fig. 28. Normal vibrations of plane YX_3 molecules

Here ν_1 is totally symmetrical; ν_3 is symmetrical about the symmetry axis but antisymmetrical with respect to the plane of the molecule; ν_2 and ν_4 are doubly degenerate, since the motion of the Y atom is isotropic in the plane of the molecule. The selection rules are as follows:

	ν_1	ν_3	ν_2 (2)	ν_4 (2)	
Infrared	inactive	$\parallel$	$\perp$	$\perp$	(86)
Raman	p	inactive	d	d	

It is seen that the plane YX_3 model differs from the pyramidal model in having only 3 active vibrations in either the absorption or the Raman spectrum.

If one now employs the less general potential (71), the condition for equilibrium is

$$\left(\frac{\partial V}{\partial r}\right)_0 + \sqrt{3}\left(\frac{\partial V}{\partial q}\right)_0 = 0. \tag{87}$$

Again on writing

$$\left(\frac{\partial^2 V}{\partial r^2}\right)_0 = k, \quad \left(\frac{\partial^2 V}{\partial q^2}\right)_0 = k_1, \quad \left(\frac{\partial V}{\partial r}\right)_0 = \frac{1}{\sqrt{3}} q\, k_2, \tag{88}$$

---

[1] The notation employed here is such that the forms of vibrations in Fig. 28 are the limiting forms of the corresponding ones in Fig. 26 for the pyramidal model when the height of the pyramid becomes zero.

the following relations between the constants $A, \ldots . E$ and k, k_1, k_2 result:

$$A = \tfrac{3}{2}\left[k + 3k_\alpha \ + k_2\right], \qquad B = 3\,(k'_\alpha + k_2),$$
$$C = \tfrac{1}{3}\ k + k_1, \qquad D = \tfrac{1}{6}\,k + \tfrac{1}{2}k_1 + \tfrac{1}{2}k_\alpha \qquad (89)$$
$$E = \ \tfrac{1}{2}k - \tfrac{3}{2}\ k_\alpha - \tfrac{1}{2}k_2,$$

For a central force potential, $k_\alpha = k'_\alpha = 0$, and the determinantal equation gives[2]

$$\lambda_1 = \frac{1}{m}(k + 3k_1), \qquad \lambda_3 = \frac{M+3m}{mM}\,k_2, \qquad (90a)$$

$$\lambda_2 + \lambda_4 = \frac{2M+3m}{2mM}\,k + \frac{3}{2m}\,k_1 + \frac{M+3m}{2mM}\,k_2,$$
$$\lambda_2 \cdot \lambda_4 = \frac{3(M+3m)}{4m^2M}\left[k\,(k_1 + k_2) + k_1\,k_2 - \tfrac{1}{3}\,k_2^2\right]. \qquad (90b)$$

For a valence force potential, $k_1 = k_2 = 0$, and one obtains

$$\lambda_1 = k/m, \qquad \lambda_3 = \frac{M+3m}{mM}\,k'_\alpha, \qquad (91a)$$

$$\lambda_2 + \lambda_4 = \frac{2M+3m}{2mM}(k + 3k_\alpha\ ), \qquad \lambda_2\,\lambda_4 = \frac{3(M+3m)}{Mm^2}\,k k_\alpha\,. \qquad (92b)$$

Corresponding to the modified valence force potential

$$2V = k\,\Sigma\,(\delta r_i)^2 + k_\alpha\ \Sigma(r\delta\alpha_i)^2 + 2k'_1 \sum_{i \neq j} \delta r_i \delta r_j + k'_\alpha\ \Sigma\left(r\ \frac{\delta S}{3}\right)^2, \qquad (92)$$

the frequencies are given by expressions obtained by replacing k in (91a) by $k + 2k'_1$, and replacing k in (91b) by $k - k'_1$.

1) BF_3, 2) BCl_3, 3) BBr_3

The Raman spectra of these molecules have been studied by Anderson, Lassettre and Yost[1]. The infrared spectrum of BF_3 has been studied by Bailey, Hale and Thompson[2], and that of BCl_3 by Cassie[3]. Electron diffraction measurements on BBr_3 and BCl_3 have been made by Wierl and by Brockway[4]. All the evidences are consistent with a plane symmetrical structure for these molecules. Because of the presence of two isotopes of boron of mass 10 and mass 11, certain vibrations show isotope splittings which are in agreement with the theoretical values. This ascertains the correctness of the assignments of the observed frequencies. The results are summarized in Table XXXV below.

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[2] Menzies, Proc. Roy. Soc. A 134, 265, (1931). The relations (90) given by H. H. Nielsen, Phys. Rev. 32, 773, (1928), are in error.

[1] Anderson, Lassettre & Yost, Jour. Chem. Phys. 4, 703, (1936); Yost, DeVault, Anderson & Lassettre, *ibid.*, 6, 427, (1938).

[2] Bailey, Hale & Thompson, Jour. Chem. Phys. 5, 274, (1937); Proc. Roy. Soc. A 161, 107, (1937).

[3] Cassie, Proc. Roy. Soc. A 148, 87, (1936).

BF_3		BCl_3		BBr_3	
ν_1	886 Ra.	ν_1	471 Ra.	ν_1	279 Ra.
ν_3	694 722 *	ν_3	462 Ra. 483 * Ra.	ν_3	371 Ra. 390 *
ν_2	1448 1501 *	ν_2	958 * 996	ν_2	806 Ra. 846 * Ra.
ν_4	440 Ra.	ν_4	243 Ra.	ν_1	151 Ra.
$2\nu_4$	862				
$\nu_3+\nu_1$	1178				
$\nu_1+\nu_4$	1370	$\nu_1+\nu_4$	714		
$\nu_2+\nu_4$	1832 1929	$\nu_2+\nu_4$	1206		
$3\nu_3$	2059	$3\nu_3$	1387 1429		
$\nu_1+\nu_2$ or $2\nu_1+\nu_4$	2251	$\nu_1+\nu_2$	1429		
$2\nu_2$	2927	$2\nu_2$	1912 1995 *		
$2\nu_2+\nu_4$	3261				
$\nu_2-\nu_4$	1038 Ra. 1105 Ra.	$r(B-Cl)=1.73$ Å		$r(B-Br)=1.87$ Å	
$2\nu_3$	1394 Ra.				

Table XXXV. Vibrational spectra of BF_3, BCl_3, BBr_3

In the table, the frequencies marked by * are due to $B^{10}X_3$. The potential constants in (92) are calculated from the four frequencies of $B^{11}X_3$ and with the constants so obtained, the frequencies for $B^{10}X_3$ can be calculated. The results are summarized in Table XXXVI.

	BF_3	BCl_3	BBr_3		$B^{10}F_3$	$B^{10}Cl_3$	$B^{10}Br_3$
k	6.69	3.30	2.50	ν_1	886	471	279
k_α	0.48	0.28	0.25	ν_3	722	483	390
k'_α	0.86	0.43	0.27	ν_2	1503	1000	843
k'_1	1.03	0.65	0.61	ν_4	441	243	151

Table XXXVI. Potential constants of BF_3, BCl_3, BBr_3 in 10^5 dy./cm.

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[4] Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

[5] Bailey, Hale and Thompson, *loc. cit.*, compared the values of the B—F, B—Cl and B—Br bond constants in these molecules with those in the respective diatomic molecules, namely, BF: $k=7.17$ (H. M. Strong & H. P. Knauss, Phys. Rev. 49, 740, 1936); BCl: $k=3.4$; BBr: $k=2.67$ (E. Miescher, Helv. Phys. Acta 8, 279, 1935).

It is seen that the calculated frequencies of $B^{10}X_3$ are in complete agreement with the observed values in Table XXXV.

4) NO_3^- ion, 5) $CO_3^=$ ion

The Raman spectra of crystals containing these ions and also of solutions have been studied by a number of authors[1]. The infrared absorption spectra and reflection spectra have been studied by Schaefer and Schubert and by Nyswandler[2]. It was found that the Raman spectra of salts containing the NO_3 ions consist of one intense line at about 1050 and two weak lines at about 720 and 1370 cm^{-1}, while the infrared spectra consist of three bands, 2 corresponding to the 720 and 1370 cm^{-1} Raman lines and one at about 835 cm^{-1}. In the case of the $CO_3^=$ ion, the Raman spectra contain one intense line in the neighborhood of 1080 cm^{-1} and two weak lines at about 710 and 1440 cm^{-1}, while the infrared spectra contain three bands, two corresponding to the two weak Raman lines and one at about 860 cm^{-1}. Infrared experiments with polarized radiations show that in both cases, only the band at 835 (or 866 in $CO_3^=$) is observed when the radiation is polarized with the electric vector parallel to the optical axis of the crystal, while the other two bands are observed when the electric vector is perpendicular to the optical axis. These results are consistent with a plane symmetrical structure, according to the selection rules (86). Below we give the fundamental frequencies of NO_3^- in $NaNO_3$, and of $CO_3^=$ in $CaCO_3$ and Na_2CO_3.

	ν_1	ν_2	$\nu_3 \parallel$	ν_4	
NO_3^-	1050	1389	835	725	(93)
$CaCO_3$	1088	1438	866	714	
Na_2CO_3	1063	1415		680	

It is of some interest to obtain the potential functions for these ions. It is found that with the frequencies in (93), equations (90) for the central force potential yield no solutions for the constants; but with the modified valence potential (92), one obtains the following values

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[1] Cf. Kohlrausch, *Der Smekal-Raman Effekt;* also Th. G. Kujumzelis, Zeits. f. Physik 109, 586, (1938); I. R. Rao, Proc. Roy. Soc. A 144, 159, (1934); R. Ananthakrishnan, Proc. Ind. Acad. Sc. A. V, 285, (1937).

[2] Cf. Cl. Schaefer and F. Matossi, *Das Ultrarote Spektrum.*

	k	k_α	k'_α	k'_1	
NO_3^-	7.05	1.28	1.27	1.77	
	6.10	1.75	1.47	2.24	
$CO_3^=$	6.15	1.55	1.41	2.06	(94)

The existence of two sets of values for the constants for NO_3^- corresponds to the quadratic nature of the equations. (In the case of $CO_3^=$, the other set has been rejected as unreasonable). It must be emphasized that the constants in (94) are meant only to give the order of magnitudes, since the frequencies from which they are obtained vary somewhat in different crystals ($NaNO_3$, KNO_3, Na_2CO_3, $CaCO_3$ etc.).

D) Plane Symmetrical ZYX_2 Molecules

A plane symmetrical ZYX_2 molecule possesses 6 normal vibrations. Of these, 5 are planar and one is antisymmetrical with respect to the plane of the molecule. Of the 5 planar vibrations, 3 are symmetrical with respect to the axis of symmetry and 2 are antisymmetrical. The general forms of these vibrations are shown in Fig. 29.

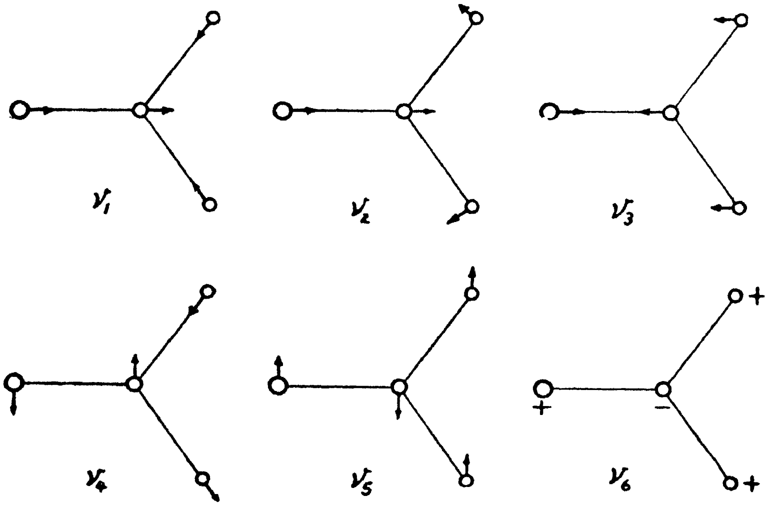

Fig. 29. Normal vibrations of OCH_2 type molecules

The selection rules are as follows:

	ν_1, ν_2, ν_3	ν_4, ν_5	ν_6
Infrared	$\mathfrak{M}_z$	$\mathfrak{M}_x$	$\mathfrak{M}_y$
Raman	p	d	d

where the z-axis is along the symmetry axis, and the y-axis perpendicular to the plane of the molecule.

The normal vibrations of such a molecule have been treated by a number of authors[1]. With a modified valence force potential of the form

$$2V=k\Big[(\delta r_1)^2+(\delta r_2)^2\Big]+k_1(\delta r)^2+k_\theta\,(a\delta\theta)^2+k_\varphi\,s^2\Big[(\delta\varphi_1)^2+(\delta\varphi_2)^2\Big]$$
$$+k_3\,\delta r\,(a\delta\theta)+k_4\delta r\,(\delta r_1+\delta r_2)\,, \tag{95}$$

the determinantal equation gives

$$\lambda_1+\lambda_2+\lambda_3=Ak+Bk_1+Ck_\alpha+Dk_3-Lk_4$$
$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1=Ekk_1+(Fk+Gk_1)\,k_\alpha+(D/m)\,k_1k_3-\tfrac{1}{2}Fk_3^2$$
$$+\left(Kk_3-\frac{L}{m}k-\tfrac{1}{2}E\,k_4\right)k_4$$
$$\lambda_1\lambda_2\lambda_3=H\,(kk_\alpha-\tfrac{1}{2}\,k_3^2)\,k_1-\tfrac{1}{2}\,H\,k_\alpha\,k_4^2 \tag{96}$$
$$\lambda_4+\lambda_5=Ck+\left(\frac{B}{a^2}+\frac{2A}{b^2}+\frac{2L}{ab}\right)s^2k_\varphi$$
$$\lambda_4\lambda_5=\left(\frac{G}{a^2}+\frac{2F}{b^2}+\frac{2L}{mab}\right)k\,k_\varphi\,s^2$$

where a=Y−X and b=Z−Y distance, and

$$A=(M+M_1)/MM_1\,,\quad B=\frac{1}{m}+\frac{2}{M}\cos^2\frac{\theta}{2}\,,\quad C=\frac{1}{m}+\frac{2}{M}\sin^2\frac{\theta}{2}\,,$$
$$D=\frac{2}{M}\sin\frac{\theta}{2}\,,\quad E=\frac{2}{M_1}B+\frac{1}{m\,M}\,,\qquad F=\frac{1}{M_1}C+\frac{1}{m\,M}\,,$$
$$G=(M+2m)/m^2M,\qquad H=(M+M_1+2m)/m^2MM_1\,,$$
$$K=\frac{2}{MM_1}\sin\frac{\theta}{2}\cos\frac{\theta}{2}\,,\qquad L=\frac{2}{M}\cos\frac{\theta}{2}.\quad k_\alpha=2k_\theta+k_\varphi\,(s/a)^2$$

The vibration ν_6 in which the atoms move in directions perpendicular to the plane of the molecule can be treated in the same manner as in the case of the perpendicular vibration of a linear triatomic molecule $2m$-M-M_1.

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[1] The equations (97) reduce to those obtained by Lechner, Wien. Ber. 141, 633, (1932), if one puts $k_3=k_4=0$; and reduce to those obtained by J. J. Fox and A. E. Martin, Proc. Roy. Soc. A 167, 257, (1938), on putting $k_4=0$.

1) OCH_2, 1a) OCD_2

The infrared spectrum of formaldehyde OCH_2 has been studied by Nielsen, Patty and Ebers[1]. On the assumption of the model in Fig. 29, and on consideration of §2, Chap. IV, the bands ν_1, ν_2, ν_3 will be of the "A" type, ν_4 and ν_5 of the "B" type and ν_6 of the "C" type. The spectrum shows 4 bands at 2974, 2780, 1744 and 1504 cm^{-1} of the $||$ type of symmetrical rotators, and 3 bands at 2865, 1287 and 1165 cm^{-1} of the $\perp$ type of symmetrical rotators. The first 3 parallel type bands have been resolved into a Q branch and a number of equidistant lines in the P and R branches, while only the contour has been mapped for the fourth. In the region of the two $\perp$ type bands at 1165 and 1287 cm^{-1}, the separations between the prominant lines (in fact groups of lines) decrease from about 24 cm^{-1} in the two outer regions of the two bands to about 5 cm^{-1} in the region between the two bands. The separations between the lines in the $\perp$ band at 2865 cm^{-1} are about 16 cm^{-1}.

The appearance of the $||$ type bands is understandable when one remembers that the OCH_2 molecule is only slightly asymmetrical, *i.e.*, $I_A \ll I_B \sim I_C$. In such a molecule, the structure of the "A" type bands would be like that of the $||$ bands of a linear molecule, but with a splitting of each line into a number of "fine structure" components, which under the practical resolution of experiment would appear as a single line. From the observed line spacings in such bands, it is possible to determine the moments of inertia of the molecule by means of the energy expressions for an asymmetrical rotator. But more accurate values are obtained from the analysis of a number of electronic bands of the molecule by Dieke and Kistiakowsky[2]. For the normal state, they found

$$I_A = 2.9, \qquad I_B = 21.4, \qquad I_C = 24.33 \times 10^{-40} \mathrm{g.\,cm}^2$$

The anomalous spacings in the $\perp$ type bands at 1165 and 1278 cm^{-1} was explained by Nielsen as due to the interaction between the vibration and the rotation of the molecule. The closeness of the frequencies of the vibrations ν_5 and ν_6 means that the motion of the C atom is only slightly anisotropic in directions perpendicular to the symmetry axis. Hence these two vibrations take on some of the properties of the doubly degenerate vibrations of molecules possessing axial symmetry, like YX_3 and ZYX_3 (see §3, Chap. IV). Nielsen[3] has worked out a calculation similar to those of Teller and of Johnston and Dennison. It was shown that the calculated structure of the two perpendicular bands ν_5 and ν_6 is in exceedingly good agreement with the observed spectrum.

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[1] J. R. Patty and H. H. Nielsen, Phys. Rev. 39, 957, (1932); H. H. Nielsen, *ibid.*, 46, 117, (1934); E. S. Ebers and H. H. Nielsen, Jour. Chem. Phys. 5, 84, 822, (1937).

[2] G. H. Dieke & G. B. Kistiakowsky, Phys. Rev. 45, 4, (1934).

The assignment of the fundamental frequencies is guided by the following considerations: Roughly speaking, ν_1 and ν_3 may be regarded as the ν_1 and ν_2 vibrations respectively in the triatomic CH_2 group and ν_2 as the vibration of the C–O group. The vibration ν_4 is roughly the ν_3 vibration in the CH_2 group. The parallel band at 2974 cm^{-1} can be assigned to the harmonic of $\nu_3=1504$, although it is possible that the two parallel bands 2780 and 2974 are jointly due to transitions from the normal state to the resonating pair of levels ν_1 and $2\nu_3$.

For OCD_2, Ebers and Nielsen[4] observed 4 || type and 3 ⊥ type bands. Only the || band at 2056 cm^{-1} and the ⊥ band at 2160 cm^{-1} have been sufficiently well resolved. The greater mass of the deuterium atom increases the asymmetry of the molecule and hence the splittings of the rotational lines, and at the same time decreases the separations between these groups of lines. The observed bands are given in Table XXXVII.

	OCH_2			OCD_2		
	Obs. ν		$\Delta\nu$	Obs. ν		$\Delta\nu$
ν_1	2780.8	∥	2.4	2056.4	∥	1.85
$2\nu_3$	2974.0	∥	2.4	2209.0	∥	
ν_2	1744.1	∥	2.4	1700	∥	
ν_3	1504	∥		1106.0	∥	
ν_4	2865	⊥	16.2	2160.3	⊥	7.6
γ_5	1278	⊥	23–5	990.2	⊥	
ν_6	1165	⊥	5–23	938	⊥	

Table XXXVII. Vibrational spectra of OCH_2 and OCD_2

The constants in the potential (96) with $k_3=k_4=0$ have been calculated by Ebers and Nielsen who found that both OCH_2 and OCD_2 can be approximately described by

$$\begin{aligned} k_{CH} &= 4.22, & k_{CO} &= 12.06, \\ k_\Theta &= 1.46, & k_\varphi (s/a)^2 &= 0.57 \times 10^5 \text{ dy./cm.} \end{aligned} \tag{97}$$

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[3] H. H. Nielsen, Jour. Chem. Phys. 5, 818, (1937); Ebers and Nielsen, *loc. cit.*

[4] E. S. Ebers and H. H. Nielsen, Jour. Chem. Phys. 6, 311, (1938).

Here one notices that the C—O bond constant is considerably lower than the value 15.9 in CO_2. The C—O bond in this case is believed to be a pure double bond, while in CO_2 it contains contributions of triple bond arising from quantum-mechanical resonance. The considerably lower value for the C—H bond constant (compared with *ca.* 5×10^5 in CH_4 and C_2H_4) must also be noted, although it is subject to changes when the observed frequencies are corrected for anharmonicity and when one takes into consideration a possible resonance interaction between ν_1 and $2\nu_3$.

2) $OCCl_2$ (phosgene)

The Raman spectrum has recently been studied by Ananthakrishnan[1] and the infrared absorption spectrum by Bailey and Hale.[2] The assignments of the observed frequencies as given by these authors are summarized by Table XXXVIII.

	Obs. ν		
Assignment	Infra.	Raman	Calc. ν
ν_1	563, 576	571 p	*
ν_2		300 p	*
ν_3	1827	1810 p	*
ν_4	845	834 d	*
ν_5		?	300
ν_6		444 d	*
$\nu_2+\nu_6$; $\nu_5+\nu_6$	735, 746		744
$2\nu_1$	1157		1152
$\nu_2+2\nu_6$			1188
$\nu_4+\nu_6$	1285		1289
$\nu_1+\nu_4$	1403		1421
$\nu_1+2\nu_6$			1452
$2\nu_1+\nu_3$			1459
$2\nu_4$	1666		1690
$\nu_2+\nu_3$; $\nu_3+\nu_5$	2062		2127
$2\nu_1+\nu_6$			2134
$\nu_1+\nu_3$	2336		2403
$\nu_3+2\nu_6$	2714		2715
?	2780		
$2\nu_3-\nu_1$	3059		3078
$2\nu_3$	3630		3654

Table XXXVIII. Vibrational spectrum of $OCCl_2$

Electron diffraction measurements give the following values for the dimensions of the molecule[3]

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[1] Ananthakrishnan, Proc. Ind. Acad. Sci. A 5, 285, (1937).

[2] C. R. Bailey & J. B. Hale, Phil. Mag. 25, 98, (1938).

[3] Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

$$r(\mathrm{C-Cl})=1.68\pm .02\ \text{Å},\quad r(\mathrm{O-C})=1.28\pm .02\ \text{Å},\quad \theta=117°\pm 2°$$

With these values and the fundamentals in Table XXXVIII, Bailey and Hale have calculated the constants in (96) with $k_3=k_4=0$,

$$k_{CCl}=2.27,\qquad k_{co}=12.1,$$
$$k_\theta=1.05,\qquad k_\varphi(s/a)^2=0.20\times 10^5\ \text{dy./cm.}\qquad (98)$$

3) $SCCl_2$ (thiophosgene)

The planar structure of this molecule is established by electron diffraction measurements which give the following dimensions[1]

$$r(\mathrm{C-Cl})=1.70\pm .02\ \text{Å},\quad r(\mathrm{S-C})=1.63\ \text{Å},\quad \theta=116°.$$

The Raman spectrum of this molecule has recently been reported by Thompson.[2] His assignments of the observed frequencies are as follows:

$$\nu_1=496\ (5),\qquad \nu_2=287\ (3),\qquad \nu_3=1121\ (10),$$
$$\nu_4=660\ (0),\qquad \nu_5=363\ (1),\qquad \nu_6=200\ (1),\qquad (99)$$
$$\nu_2+\nu_3=1388\ (2).$$

E) Pyramidal YZX_2 Molecules

A molecule with a Y atom at the vertex of a pyramid and a Z atom and two X atoms forming an isoceles triangle at the base has the symmetry C_s. Of the 6 normal vibrations, 4 are symmetrical with respect to the plane of symmetry (containing Y and the bisector of the angle X—Z—X), and 2 are antisymmetrical. In case the bindings between the Y atom and the Z, X atoms are stronger than those between the Z and X and between the X atoms themselves, the nature of the vibrations can be roughly described as follows. Of the 4 symmetrical vibrations, one involves the symmetrical valence vibration ν_1 in the YX_2 group, one the valence vibration in the Y—Z bond, one the symmetrical deformation vibration ν_2 in YX_2, and the other a deformation vibration of the triangular system Z—Y—(X_2). Of the antisymmetrical vibrations, one involves the valence vibration ν_3 in YX_2, and the other a deformation vibration of the molecule. All the vibrations are active in both the absorption and the Raman spectra, with the symmetrical vibrations polarized and the antisymmetrical vibrations depolarized.

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[1] Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

[2] H. W. Thompson, Jour. Chem. Phys. 6, 748, (1938).

1) OSF_2 (thionyl fluoride), 2) $OSCl_2$ (thionyl chloride)

The Raman spectrum of these molecules are known.[1] The following assignments can be made on considerations of the valence frequencies in SO_2, SF_2, O_2SCl_2 (see sections on these molecules in this chapter).

	$\nu(S-O)$	$\nu_1(SX_2)$	$\delta(SX_2)$	$\delta(OSX_2)$	$\nu_3(SX_2)$	δ	
OSF_2	1312(10)	720(9)	529(8)	395(6)	795(9)	326(1)	(100)
$OSCl_2$	1229(*m*)	443(*s*)	343(*vs*)	282(*s*)	488(*s*)	192(*s*)	

§3. Penatomic Molecules

A) Linear Symmetrical Y_3X_2 Molecule

The only molecule of the form X-Y-Y-Y-X known is carbon suboxide C_3O_2. This molecule possesses 10 vibrational degrees of freedom. Simple symmetry considerations show that there are 4 parallel vibrations of which 2 are symmetrical and 2 antisymmetrical with respect to the center of symmetry, and 3 doubly degenerate vibrations of which one is symmetrical and 2 are antisymmetrical with respect to the center of symmetry. The general forms of these vibrations are shown in Fig. 30.

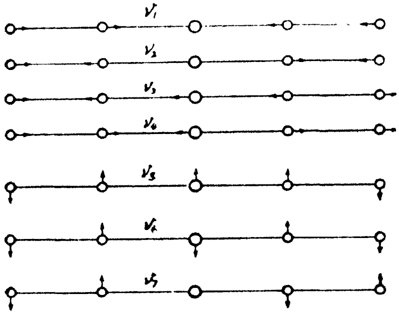

Fig. 30. Normal vibrations of carbon suboxide molecule

The selection rules are as follows:

	ν_1, ν_2	ν_3, ν_4	ν_5, ν_6	ν_7
Infrared	Inactive	$\parallel$	$\perp$	inactive
Raman	p	inactive	inactive	d

The normal vibrations can be treated in the same way as for the C_2H_2 type molecules. For the parallel vibrations, let the changes in the lengths of the 4 successive bonds be x_1, x_2, x_3, x_4 and let us assume a potential of the form

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[1] OSF_2, Best & Trampe, quoted by Don M. Yost, *Raman Jubilee Volume*, Proc. Ind. Acad. Sci. A. (1938); $OSCl_2$, Matossi-Aderhold, Nisi, in Kohlrausch, *Der Smekal-Raman Effekt*, P. 349.

$$2V = k_1(x_2^2 + x_3^2) + k_2(x_1^2 + x_4^2) + 2k_3(x_1 x_2 + x_3 x_4) + 2k_4 x_2 x_3 \tag{101}$$

The determinantal equation gives for the 2 symmetrical vibrations

$$\begin{aligned} \lambda_1 + \lambda_2 &= \frac{1}{M}(k_1 + k_4) + \left(\frac{1}{m} + \frac{1}{M}\right) k_2 - \frac{2}{M} k_3 \\ \lambda_1 \lambda_2 &= \frac{1}{mM}\left[(k_1 + k_4) k_2 - k_3^2\right], \end{aligned} \tag{102a}$$

and for the 2 antisymmetrical vibrations

$$\begin{aligned} \lambda_3 + \lambda_4 &= \frac{3}{M}(k_1 - k_4) + \left(\frac{1}{m} + \frac{1}{M}\right) k_2 - \frac{2}{M} k_3 \\ \lambda_3 \lambda_4 &= \frac{3M + 2m}{mM^2}\left[(k_1 - k_4) k_2 - k_3^2\right] \end{aligned} \tag{102b}$$

For the perpendicular vibrations, let us choose a potential of the form

$$2V = k_{\alpha 1}(\alpha_1^2 + \alpha_3^2) + k_{\alpha 2}\alpha_2^2 + 2k_{\alpha 3}(\alpha_1 \alpha_2 + \alpha_2 \alpha_3). \tag{103}$$

The symmetrical vibration is given by

$$M\left[1 + \frac{Mb^2}{m(a+b)^2}\right]\lambda_7 = k_{\alpha 1}\left[\frac{1}{a} + \frac{1}{b} + \frac{Mb}{a(a+b)m}\right]^2, \tag{104a}$$

and the 2 antisymmetrical vibrations are given by

$$(\beta\gamma - \delta^2)\lambda_{5,6}^2 - [\gamma k_{\alpha 1} + \tfrac{1}{2}\beta k_{\alpha 2} - 2\delta k_{\alpha 3}]\lambda_{5,6} + \tfrac{1}{2}[k_{\alpha 1} k_{\alpha 2} - 2k_{\alpha 3}^2] = 0 \tag{104b}$$

where

$$\beta = r^2\left[m\left(\frac{M+2m}{M}\right)\left(\frac{6}{b}\right)^2 - 3M\left(\frac{4m}{Mb}\right)^2\right],$$

$$\gamma = r^2\left[m\left(\frac{M+2m}{M}\right)\left(\frac{1}{a} + \frac{3}{b}\right)^2 + 4m\left(\frac{1}{a} + \frac{3}{b}\right)\left(\frac{1}{a} - \frac{2m}{Mb}\right) + 3M\left(\frac{1}{a} - \frac{2m}{Mb}\right)^2\right],$$

$$\delta = r^2\left[-m\left(\frac{M+2m}{M}\right)\left(\frac{1}{a} + \frac{3}{b}\right)\frac{6}{b} + \frac{4m}{ab}\left(\frac{2m}{M} - 3\right) + \frac{48m^2}{Mb^2} + 3M\left(\frac{4m}{Mb}\right)\left(\frac{1}{a} - \frac{2m}{Mb}\right)\right],$$

$$r = \frac{Mab}{2(3M + 2m)}.$$

The infrared absorption spectrum of C_3O_2 has been studied by Lord and Wright[1], and the Raman spectrum by Engler and Kohlrausch[2].

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[1] R. C. Lord & N. Wright, Jour. Chem. Phys. 5, 642, (1937).

[2] W. Engler and K. W. F. Kohlrausch, Zeits. f. phys. Chem. B 34, 214, (1936).

The assignments of the fundamental frequencies have been discussed by the former authors on the basis of the selection rules for a linear symmetrical model (similar to those for C_2H_2). There is little doubt that $\nu_2(s)=843$ Ra., $\nu_1(s)=2200$ Ra., $\nu_4(a)=1570$ Inf., $\nu_3(a)=2290$ Inf., $\nu_7(s)=586$ **Ra.** As to the two antisymmetrical deformations ν_5 and ν_6, these authors found that it is possible to account satisfactorily for all the observed bands on the basis of two alternative assumptions: $\{\nu_5(a)=190,\ \nu_6(a)=550\}$, or $\{\nu_5(a)=190,\ \nu_6(a)=900\}$. The observed bands and their assignments are given in Table XXXIX.

		$\nu_6(a)=550$		$\nu_6(a)=900$	
Obs.		Assignment	Calc.	Assignment	Calc.
550		ν_6	*	$3\nu_5$	
586	Ra.	ν_7	*	ν_7	*
630		$\nu_2-\nu_5$	650	$\nu_2-\nu_5$	650
779		$\nu_5+\nu_7$	780	$\nu_5+\nu_7$	780
843	Ra.	ν_2	*	ν_2	*
909		$\nu_6+2\nu_5$	930	ν_6	*
1024		$\nu_2+\nu_5$	1030	$\nu_2+\nu_5$	1030
1126		$\nu_6+\nu_7$	1140	$3\nu_5+\nu_7$	1140
1225		$\nu_2+\nu_7-\nu_5$	1240	$\nu_2+\nu_7-\nu_5$	1240
1387		$\nu_2+\nu_6$	1390	$\nu_2+3\nu_5$	1390
1470		$2\nu_2-\nu_5$	1500	$\nu_6+\nu_7$	1490
1570		ν_4	*	ν_4	*
1670		$\nu_6+2\nu_7$?	1720	$3\nu_5+2\nu_7$	1720
1760		,, ?	1720	$\nu_2+\nu_6$	1740
1850		$2\nu_2+\nu_5$?	1880	$2\nu_1+\nu_5$	1880
		$\nu_3-2\nu_5$?	1910	$\nu_3-2\nu_5$	1910
1980		$\nu_1-\nu_5$	2010	$\nu_5+2\nu_6$	1990
2190		$\nu_4+\nu_7$	2160	$\nu_6+2\nu_7$	2070
2200	Ra.	ν_1	*	ν_1	*
2290		ν_3	*	ν_3	*
2410		$\nu_1+\nu_5$?	2390	$\nu_1+\nu_5$?	2390
		$\nu_2+\nu_4$	2410	$\nu_2+\nu_4$	2410
3150		$\nu_2+\nu_3$	3130	$\nu_2+\nu_3$	3130
3380		$\nu_3+2\nu_6$	3390	$2\nu_6+\nu_4$	3370
3790		$\nu_1+\nu_4$	3770	$\nu_1+\nu_4$	3770
4590		$\nu_1+\nu_3$	4490	$\nu_1+\nu_3$	4490

Table XXXIX. Vibrational spectrum of C_3O_2

It is seen that it is not possible to decide between the two alternative assumptions regarding $\nu_6(a)$. From the 4 parallel fundamentals, the constants in the potential (101) can be calculated,

$$k_{CC} = 12.5, \qquad k_{CO} = 16.0, \qquad k_3 = 2,6, \qquad k_4 = 1.42. \qquad (105)$$

It is noted that the C–O bond constant is considerably higher than the value 12×10^5 in OCH_2, but is about the same as in CO_2. This again suggests contributions from triple bond wave functions as the result of resonance among the following structures

$$\overset{+}{\mathrm{O}}-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\overset{-}{\mathrm{O}},\qquad \mathrm{O}=\mathrm{C}=\mathrm{C}=\mathrm{C}=\mathrm{O},\qquad \overset{-}{\mathrm{O}}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\overset{+}{\mathrm{O}}$$

Electron diffraction measurements show, however, that the C-O distance 1.20±.02 Å is greater than the value 1.13 Å in CO_2 and 1.15±.05 Å in OCH_2.[3]

The constants in the potential (103) can be calculated for both assignments $\nu_6(a)=550$ and $\nu_6(a)=900$.

$$\begin{array}{llll}
 & k_{\alpha 1} = 0.82 & & \\
(\mathrm{I})\ \ \nu_5 = 190 & \left\{\begin{array}{l} k_{\alpha 2} = \ \ 2.12, \\ k_{\alpha 3} = -0.85, \end{array}\right. & \text{or} & \left\{\begin{array}{l} k_{\alpha 2} = \ \ 0.47, \\ k_{\alpha 3} = -0.22; \end{array}\right. \\
\phantom{(\mathrm{I})}\ \ \nu_6 = 550 & & & \\
(\mathrm{II})\ \nu_5 = 190 & \left\{\begin{array}{l} k_{\alpha 2} = \ \ 3.94, \\ k_{\alpha 3} = -1.1\ , \end{array}\right. & \text{or} & \left\{\begin{array}{l} k_{\alpha 2} = 0.95, \\ k_{\alpha 3} = 0.04\times 10^{-11}. \end{array}\right. \\
\phantom{(\mathrm{II})}\ \nu_6 = 900 & & &
\end{array} \tag{106}$$

For each assignment, two sets of constants are obtained because of the quadratic nature of (104b). The first set in each case can almost be immediately excluded since they are very much higher than similar deformation constants in other molecules. Of the second sets, not much can be said except that the assignment $\nu_6=900$ seems to be more in line with the general result in other molecules (C_2H_2, C_2N_2, C_4H_2) that the interaction term is in general considerably smaller than the main terms in the potential.

B) Tetrahedral YX_4 Molecules

Consider a molecule consisting of 4 X atoms at the corners of a regular tetrahedron and a Y atom at the center. Because of the high symmetry, the nine degrees of freedom for vibration degenerate into four distinct frequencies: ν_1 which consists in a symmetrical pulsation of the 4 X atoms about the center; ν_2 in the motions of the X atoms in directions perpendicular to the Y-X bonds and is doubly degenerate since the motion of any X atom is isotropic in directions perpendicular to the Y-X bond; ν_3 which may be roughly described as the out-of-phase ν_1 vibrations in the two YX_2 groups (the in-phase vibrations give ν_1 above); and ν_4 which is roughly the vibration of the Y atom with respect to the 4 X atoms as a whole. The vibrations ν_3 and ν_4 are tribly degenerate in a first approximation in which the motion of the Y atom is isotropic about its position of equilibrium. The general forms of the vibrations are shown in Fig. 31.

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[3] $r(C-C)=1.29\pm.03$Å, $r(C-O)=1.20\pm.02$A. Cf. L. O. Brockway, Rev. Mod Phys. 8, 231, (1936).

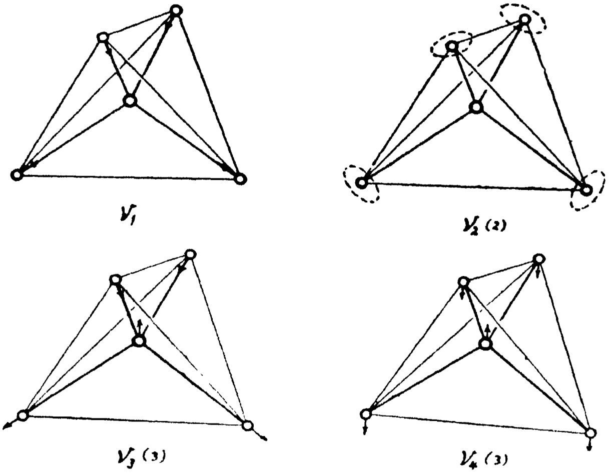

Fig. 31. Normal vibrations of tetrahedral YX_4 molecules

The selection rules are as follows: For the fundamentals,

	ν_1	ν_2 (2)	ν_3 (3)	ν_4 (3)	
Infrared	inactive	inactive	active	active	(107)
Raman	p	d	d	d	

and for harmonic and combination bands,

$$\text{Infrared} \quad \Delta v_1, \quad \Delta v_2, \quad \text{arbitrary}, \quad |\Delta v_3| + |\Delta v_4| \neq 0$$

$$\text{Raman} \quad \Delta v_1, \quad \Delta v_2, \quad \Delta v_3, \quad \Delta v_4 \quad \text{arbitrary}. \tag{107a}$$

The order of magnitude of the normal frequencies can be obtained from the above considerations of the nature of the vibrations. In general, ν_1 and ν_3 are more or less characteristic of the Y-X valence vibration frequency while ν_2 and ν_4 have low values. A treatment of the normal vibrations of the YX_4 molecule was first given by Dennison[1] who assumed a central force potential. On the other hand, a treatment based on a simple valence force potential was given by Lechner[2]. It has been shown by Rosenthal[3] that the most general potential function having the same symmetry as the tetrahedral symmetry of the molecule contains five constants A, B, C, D, E, and that the determinantal equation gives for the 4 distinct frequencies

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[1] D. M. Dennison, Astrophys. Jour. 62, 84, (1925).

$$\begin{aligned} \lambda_1 &= 16\, E/m, & \lambda_2 &= 4\, C/m. \\ m\,(\lambda_3 + \lambda_4) &= \left(\frac{1}{4\mu} A + 8B \right), & m^2\lambda_3\lambda_4 &= \frac{2}{\mu}\,(AB - D^2), \end{aligned} \tag{108}$$

where $\mu = M/(M+4m)$. The meaning of these potential constants can be made clear by the following relations between them and the constants in the potential

$$\begin{aligned} 2V &= K_1 \sum_{i,j} \tfrac{1}{2}\,(\delta q_{ij})^2 + K_2 \sum_{i,j,n\neq 1} \tfrac{1}{2}\,\delta q_{1i}\,\delta q_{jn} + K_3 \sum_i (\delta r_i)^2 \\ &\quad + K_4 \,(\sum_i \delta r_i)^2 + K_5 \sum_{i,j,n} \tfrac{1}{2}\,\delta r_i\; \delta q_{jn}, \end{aligned} \tag{109}$$

where q, r are the X–X and Y–X distances respectively. The relations are

$$\begin{aligned} A &= \tfrac{4}{3}\, K_3, & B &= \tfrac{1}{4}\, K_1 - \tfrac{1}{8}\, K_2 + \tfrac{1}{12} K_3 - \frac{1}{2\sqrt{6}} K_5\,, \\ C &= \tfrac{1}{4}\,(K_1 + \tfrac{1}{2}\, K_2), & D &= \tfrac{1}{3}\, K_3 - \frac{1}{\sqrt{6}}\, K_5\,, \\ E &= \tfrac{1}{4}\,[K_1 + \tfrac{1}{2} K_2 + \tfrac{1}{4}\, K_3 + K_4 + \sqrt{\tfrac{3}{2}}\, K_5]. \end{aligned} \tag{110}$$

As there are five constants in the potential but only four distinct frequencies, it is necessary for practical purposes to employ a less general potential containing fewer constants. A potential containing central and valence forces is the following:

$$\begin{aligned} 2V = \left(\frac{\partial V}{\partial q} \right)_0 \Sigma\, \delta q_{ij} + 2\left(\frac{\partial V}{\partial r} \right)_0 \Sigma\, \delta r_i + \left(\frac{\partial^2 V}{\partial r^2} \right)_0 \Sigma\, (\delta r_i)^2 + \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial q^2} \right) \Sigma (\delta q_{ij})^2 \\ + \tfrac{1}{2} k_\alpha\, \Sigma\, (r \delta \alpha_{ij})^2 \end{aligned} \tag{111}$$

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[2] F. Lechner, unpublished *Graz Dissertation.*

[3] J. E. Rosenthal, Phys. Rev. 45, 538, 766; 46, 730, (1934).

where α_{ij} is the angle between r_i and r_j.

The condition for equilibrium is

$$\left(\frac{\partial V}{\partial r}\right)_0 = -\sqrt{6}\left(\frac{\partial V}{\partial q}\right)_0$$

On writing

$$\left(\frac{\partial^2 V}{\partial r^2}\right)_0 = k, \quad \left(\frac{\partial^2 V}{\partial q^2}\right)_0 = k_1, \quad \left(\frac{\partial V}{\partial q}\right)_0 = q\,k_2, \tag{112}$$

one obtains

$$A = \tfrac{4}{3}\,(k + 4k_\alpha - 8k_2)\,, \qquad B = \tfrac{1}{12}(k + k_\alpha + 3k_1 + k_2)\,,$$

$$C = \tfrac{1}{4}(3k_\alpha + k_1 - k_2)\,, \qquad D = \tfrac{1}{8}(k - 2k_\alpha + 4k_2),$$

$$E = \tfrac{1}{16}(k + 4k_1)\,. \tag{113}$$

In this case, only 4 of the 5 constants A, B, C, E, D are independent, there being one relation among them

$$D = 10\,B - 2\,C - 8\,E \tag{113a}$$

From (113) one obtains

$$k = \tfrac{1}{4}A + 20\,B - 4\,C - 16\,E, \qquad k_\alpha = 3\,B + C - 4\,E,$$

$$k_1 = -\tfrac{1}{16}A - 5\,B + C + 8\,E, \qquad k_2 = -\tfrac{1}{16}A + 4\,B - 4\,E. \tag{114}$$

With the potential (111), it is possible to express the constant D in terms of the 4 frequencies by means of (113a) and (108),

$$\frac{1}{m}\left(1 + \frac{25}{8\mu}\right) D = \tfrac{5}{8}\,(\lambda_3 + \lambda_4) - \left(\frac{\lambda_1 + \lambda_2}{2}\right) \pm \tfrac{5}{8}\Big[\left(1 + \frac{25}{8\mu}\right)(\lambda_3 - \lambda_4)^2$$

$$- \frac{2}{\mu}\left\{\tfrac{5}{4}\,(\lambda_3 + \lambda_4) - (\lambda_1 + \lambda_2)\right\}^2\Big]^{\frac{1}{2}} \tag{115}$$

and by means of (108),

$$A = 2m\mu\left\{\lambda_3 + \lambda_4 \pm \left[\,(\lambda_3 - \lambda_4)^2 - \frac{8}{\mu m^2}\,D^2\right]^{\frac{1}{2}}\right\}\,,$$

$$B = \frac{m}{16}\left\{\lambda_3 + \lambda_4 \mp \left[\,(\lambda_3 - \lambda_4)^2 - \frac{8}{\mu m^2}\,D^2\right]^{\frac{1}{2}}\right\}\,, \tag{116}$$

$$C = m\,\lambda_2/4, \qquad E = m\,\lambda_1/16.$$

On the assumption of a central field, $k_\alpha=0$ and (108) become, on account of (113),

$$\lambda_1 = (k + 4k_1)/m\,, \qquad \lambda_2 = (k_1 - k_2)/m\,,$$

$$\lambda_3 + \lambda_4 = \frac{3M+4m}{3mM}\,k + 2\,\frac{1}{m}k_1 - \frac{2(3M+16m)}{3mM}\,k_2, \tag{117}$$

$$\lambda_3\lambda_4 = \frac{2(M+4m)}{3m^2M}\Big[\,k\,(k_1 - 5k_2) - 8k_2\,(k_1 + k_2)\,\Big]$$

For a simple valence force potential, $k_1=k_2=0$, and (108) become in this case

$$\lambda_1 = k/m\,, \qquad \lambda_2 = 3k_\alpha/m\,,$$

$$\lambda_3 + \lambda_4 = \left(\frac{4}{3M} + \frac{1}{m}\right)k + 2\left(\frac{8}{3M} + \frac{1}{m}\right)k_\alpha, \tag{118}$$

$$\lambda_3\lambda_4 = \frac{2}{m}\left(\frac{4}{M} + \frac{1}{m}\right)kk_\alpha.$$

From (118), the following relations result:

$$\lambda_1\lambda_2 = \frac{3\mu}{2}\lambda_3\lambda_4 \quad ; \quad \lambda_3+\lambda_4 = \tfrac{1}{8}\left[(2 + \frac{1}{\mu})\,\lambda_1 + \tfrac{2}{3}\,(1 + \frac{2}{\mu})\,\lambda_2\,\right]. \tag{119}$$

These two relations may be used as a criterion as to whether a molecule can be satisfactorily described by a simple valence force potential.

A special form of the potential (111) has been suggested by Urey and Bradley[4] who assumed a potential k'_3/q^n for two X–atoms. On this assumption, (111) can be put in the form

$$V = \left(\frac{nk'_3}{q^{n+1}}\right)\Sigma\,(\sqrt{6}\,\delta r_i - \delta q_i) + \tfrac{1}{2}\Sigma\left(\frac{\partial^2 V}{\partial r^2}\right)(\delta r_i)^2 + \tfrac{1}{2}\,k_\Theta\,\Sigma\,(r\delta\theta_i)^2$$

$$+ \tfrac{1}{2}\,\frac{n(n+1)}{q}\,k'_3\,\Sigma\,(\delta q_i)^2, \tag{120}$$

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[4] H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969, (1931).

where n is a positive integer, and θ_i is the angle of deviation of the $Y-X_i$ bond from its position of equilibrium. The equations for the frequencies are

$$m\lambda_1 = k + (n+1)k_3; \quad m\lambda_2 = k_\theta + \tfrac{1}{2}(n+2)k_3,$$

$$3m(\lambda_3+\lambda_4) = \left(3+\frac{4m}{M}\right)k + \left(3+\frac{8m}{M}\right)k_\theta + \left(1+\frac{3n}{2}+\frac{2m}{\mu}\right)k_3, \qquad (121)$$

$$3m\mu\lambda_3\lambda_4 = 3\,k\,k_\theta + (3+\tfrac{1}{2}n)\,k\,k_3 + n\,k_\theta\,k_3 + n\,k_3^2,$$

where

$$k = \left(\frac{\partial^2 V}{\partial r^2}\right), \quad k_3 = 4nk_3'/q^{n+2}, \quad \mu = mM/(M+4m). \qquad (122)$$

As has been pointed out by Rosenthal, the assumption above concerning the force between the X atoms is equivalent to setting $k_1 = -(n+1)k_2$ in (112).

For the harmonic and combination bands, it is necessary to take into consideration the effect of anharmonicity of the vibrations. It has been shown in §1, D, Chap. III, that on account of the symmetry of the YX_4 molecule, the state v_3 or v_4 is degenerate, the degree of degeneracy being

$$\tfrac{1}{2}(v+1)(v+2). \qquad (123)$$

A part of this degeneracy is removed if an anharmonic potential having tetrahedral symmetry is introduced. The number of distinct levels into which a state v (v_3 or v_4) is split has been given in Table I. The magnitude of the splitting separations between the levels of a given state v depends on the anharmonic potential and the masses of the atoms in the molecule. Hence the first harmonic of the fundamental ν_3 or ν_4 would consist of three component bands, the third harmonic seven component bands, etc., of which, however, not all are active in absorption.

The rotational structure of the infrared active bands would according to §§ 1, 2, Chap. IV, consist of a number of equidistant lines with the separation $\Delta\nu = h/4\pi^2 I$, where I is the moment of inertia of the molecule. The structure which is observed in the bands of such molecules as CH_4 is, however, much more complicated than is predicted by this simple theory. The complexity of the band structure can be explained on the following considerations:

(*i*) The theory of Teller and of Johnston and Dennison,[5] §4, Chap. IV, shows that the interaction between the vibration and the rotation of molecules possessing 3-fold axis of symmetry gives rise to energy changes which are different for different states of the degenerate vibrations. Recently, Jahn[6] has published a detailed study of this type of interaction in the YX_4 molecules.

(*ii*) As a result of the splitting of a band involving harmonics or combinations of the tribly degenerate fundamental ν_3 or ν_4 into a number of component bands, unless the splitting separations are large, these component bands will overlap one another, resulting in a high complexity in the rotational structure of the band.

1) CH_4

The infrared and the Raman spectra of CH_4 have been studied by a number of authors[1,2,3]. The observed frequencies are summarized in Table XL.

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[5] D. M. Dennison & S. B. Ingram, Phys. Rev. 36, 1451, (1930); also M. Johnston & D. M. Dennison, *ibid.*, 48, 868, (1935).

[6] H. A. Jahn, Proc. Roy. Soc. A 168, 469, 495, (1938); W. H. J. Childs and Jahn, *ibid.*, 169, 451, (1939). In these papers, the effect of the coupling between the vibrations $\nu_2(2)=1520$ and $\nu_4(3)=1305$ on the positions and the intensities of the rotational lines in the ν_4 band is worked out. The result is in complete agreement with the observed structure of the band measured by A. H. Nielsen & H. H. Nielsen, Phys. Rev. 48, 864, (1935).

[1] Infrared bands: J. P. Cooley, Astrophys. Jour. 62, 73, (1925), 1305 and 3022 cm^{-1} bands under high dispersion; J. W. Ellis, Proc. Nat. Acad. Sci. 13, 202, (1927), near infrared bands under low dispersion; J. G. Moorhead, Phys. Rev. 39, 83, (1932); W. V. Norris & H. J. Unger, *ibid.*, 43, 467, (1933); A. H. Nielsen & H. H. Nielsen, *ibid.*, 48, 864, (1935), near infrared bands resolved into rotational lines.

[2] Photographic bands: R. Mecke, Zeits. f. Astrophys. 6, 144, (1933); H. Vedder and R. Mecke, Zeits. f. Physik 86, 137, (1933); D. M. Dennison & S. B. Ingram, Phys. Rev. 36, 1451, (1930), 11620 cm^{-1} band; W. H. J. Childs, Proc. Roy. Soc. A 153, 555, (1935), 8900 and 9047 cm^{-1} bands.

[3] Raman spectrum: Dickenson, Dillon & Rasetti, Phys. Rev. 34, 582, (1929); C. M. Lewis & W. V. Houston, Phys. Rev. 44, 903, (1933); Polarization measurements by S. Bhagavantam, Nature 129, 830, (1932).

Assignment	Obs. ν		$\Delta\nu$ in cm^{-1}		Calc. ν
			Obs.	Calc.	
ν_1	2915	Ra.			*
ν_2	(1520)				*
ν_3	3019.6 3022	 Ra.	9.77	*	*
ν_4	1305		5.4	*	*
$2\nu_4$	2608		15.3	14.8	*
$\nu_2+\nu_4$	2824				
$2\nu_2$	3072	Ra.			
$\nu_2+2\nu_4$	4122				*
$\nu_1+\nu_4$	4218		5.3	5.4	*
$\nu_3+\nu_4$	4315		13.5	12.6	*
$\nu_2+\nu_3$	4547		10.7	9.8	4534
$\nu_3+2\nu_4$	5588		10.2	14.8	5610
$\nu_2+\nu_3+\nu_4$	5769		10.85	12.6	5826
$\nu_1+\nu_3$	5865			9.77	5870
$2\nu_3$	6008		10.4	10.5	*
$\nu_2+2\nu_3$	7516		10.65	10.5	*
$2\nu_1+2\nu_4$	8423		10.86	14.8	
$2\nu_1+\nu_3$	8606		9.44	9.77	8626
$\nu_1+2\nu_3$	8800			10.5	*
	8900				
$2\nu_3$	9017		10—11	9.77	8964
$2\nu_1+\nu_2+\nu_3$	10114			9.77	*
$\nu_1+\nu_2+2\nu_3$	10303			10.5	10296
$3\nu_1+\nu_3$	11270			9.77	*
$2\nu_1+2\nu_3$ or $\nu_1+3\nu_3$	11620				
$4\nu_3$	11885				11888
$3\nu_1+\nu_2+\nu_3$	12755				12775
$4\nu_1+\nu_3$	13790				13839

Table XL. Vibrational spectrum of CH_4

The assignments of the observed bands are based on considerations of the rotational line spacings according to the theory of Teller and of Johnston and Dennison.[4] From the spacings of the rotational lines in ν_3 and ν_4 and by means of (83) and Table IV of Chap. IV, the latter authors obtained the following dimensions

$$I=5.47\times 10^{-40}\,\text{g.cm}^2,\quad r\,(C-\text{H})=1.11\ \text{Å},\quad r\,(\text{H}-\text{H})=1.81\ \text{Å}. \qquad (124)$$

The spacings in the other bands calculated according to (89) of Chap. IV are in reasonable agreement with the observed values.

From the bands marked by *, an estimate is made of the coefficient in the energy expression

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[4] M. Johnston & D. M. Dennison, Phys. Rev. 48, 868, (1935).

$$E/h=(v_1+\tfrac{1}{2})\nu_1+(v_2+1)\nu_2+(v_3+\tfrac{3}{2})\nu_4+(v_4+\tfrac{3}{2})\nu_4+(v_1+\tfrac{1}{2})^2x_{11}$$

$$+\cdots\cdots(v_8+\tfrac{3}{2})(v_4+\tfrac{3}{2})x_{84}$$

which is not strictly correct since it takes no account of the removal of the degeneracy (123). For the same reason, the frequencies calculated for the other bands are only approximate. Nevertheless, such a calculation serves to show that the assignments for most of the bands are correct.

The spectrum of CH_4 is of special interest in another connection. Some 40 bands in the visible and the photographic infrared regions have been observed in the absorption spectra of the atmospheres of the major planets; and these bands have been identified as CH_4 bands by studying the spectrum of the gas under high pressure in a long tube. This shows that the atmospheres of Jupiter, Uranus and Neptune contain enormous amounts of methane.[5]

To obtain the potential function of the CH_4 molecule, Johnston and Dennison[4] have obtained the following relations between the constants A and D in (108) and the rotational line spacings in ν_8 and ν_4,

$$\Delta\nu_i=(1-\xi_i)\frac{h}{4\pi^2I}\ ,\qquad \xi_i=\frac{(6\,\delta_i-1)}{(6\,\delta_i+2)}\ ,\qquad \delta_i=\frac{8D^2}{(3m\,\lambda_i-A)^2}\,. \tag{125}$$

From these and (108), they found the following values[6]

$$A=7.67,\quad B=0.476,\quad C=0.341,\quad D=1.278,\quad E=0.313 \tag{126}$$

From (114), the potential constants in the potential (111) are obtained,

$$k_{CH}=5.07,\quad k_\alpha=0.50,\quad k_{HH}=-0.15,\quad k_2=0.17. \tag{127}$$

The smallness of the values for k_{HH} and k_2 compared with k_{CH} and k_α shows that the simple valence force potential is a good approximation, as can also be seen by putting the frequencies into (119). The central force potential is, however, not as satisfactory since k_α turns out to be greater than k_{HH} and k_2.

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[5] A, Adel and V. M. Slipher, Phys. Rev. 46, 240, 902, (1934); 47, 651, 787, (1935). The classification of the major planet bands given by them is based on the assignment $3\nu_8=8606$ cm^{-1}. According to the scheme in Table XL, it would be necessary to change $n\nu_8$ into $(n-1)\nu_1+\nu_8$.

[6] On account of the quadratic nature of the equation for D in (108), two roots were obtained, namely, $D=\pm1.278\times10^5$. The negative value is rejected since the frequencies calculated with it for the deuteromethanes do not agree with the observed values (see below).

1a, 1b, 1c, 1d) CH_3D, CH_2D_2, CHD_3, CD_4

The spectra of these deutero-methanes are of interest for the following reasons: (1) the substitution of one, two or three of the H atoms in CH_4 by the D atoms lowers the symmetry of the molecule and removes a part or all of the degeneracy in the vibrational motion of the molecule. Thus CH_3D and CHD_3 have only a 3-fold axis of symmetry and there are in each molecule 6 normal vibrations of which 3 are doubly degenerate; while CH_2D_2 has nine completely non-degenerate vibrations.[1] From these frequencies of the isotopic molecules and on the very reasonable assumption that the potential function remains unchanged by the isotope substitution, one can obtain more information concerning the potential of the molecule than from the spectrum of CH_4 alone, and (2) the study of the spectra of these isotopic molecules has offered a means for the investigation of the equilibrium of reactions involving isotope exchange.[2] The fact that each of the molecules possesses a spectrum different from those of the others has made possible the analysis of isotope mixtures. In the following, we shall only be concerned with the spectra of these molecules in so far as they furnish information concerning their structure, and reference must be made to the literature for the more chemical aspects of the problem.

The infrared absorption spectra of these deutero-methanes have been examined by Benedict, Barnes and their coworkers under rather low dispersion.[2] They located nearly all the fundamental bands although no rotational structure was obtained. The Raman spectra of these molecules have been studied by McWood and Urey.[3] The infrared spectrum of CH_3D has been studied under high dispersion by Ginsberg and Barker,[4] and the spectrum of CD_4 has been studied by Nielsen and Nielsen.[5] The observed frequencies of these molecules are summarized in Table XLI.

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[1] For the modes of these vibrations, see Figs. 32 and 33 below.

[2] W. S. Benedict, K. Morikawa, R. B. Barnes & H. S. Taylor, Jour. Chem. Phys. 5, 1, (1937).

[3] G. E. McWood & H. C. Urey, *ibid.*, 3, 65, (1935); 4, 402, (1936); A. Dadieu & W. Engler, Naturwiss. 23, 355, (1935), gave 2108 and 2141 cm^{-1} for CD_4.

[4] N. Ginsberg & E. F. Barker, Jour. Chem. Phys. 3, 668, (1935).

[5] H. H. Nielsen, Phys. Rev. 51, 62, (1937); H. H. Nielsen, & A. H. Nielsen, ibid., 54, 118, (1938).

		ν_1	$\nu_2(2)$		$\nu_3(3)$			$\nu_4(3)$		
CH_4	Inf.					3019.6			1306	
	Ra.	2915	1520			3022				
	Calc.	*	1520 *			*			*	
CH_3D	Inf.	2983	1477.1		3031		2205	1156		1307
	Ra.		(2921.7)				2199.5	(2314.8)		1330
	Calc.	2961	1458		3032		2193	1147		1311
CH_2D_2	Inf.		1450			2255	3020	1036	1235.5	1090.5
	Ra.	2139	(2916)	1285.6	2974			1033	1333	(2179)
	Calc.	2144	1450	1290	2980	2265	3027	1038	1227	1085
CHD_3	Inf.		1290		2260		3000	988		988
	Ra.	2141	1299.2		2268.6			(1963.4)		(2092.8)
	Calc.	2127	1293		2263		3015	995		997
CD_4	Inf.					2259			995.86	
	Ra.	2085				2258				
	Calc.	*	1052			*			*	

Table XLI. Fundamental frequencies of deutero-methanes. The Raman frequencies in parentheses are the observed first harmonics of the respective vibrations

The assignments of the frequencies of the deutero-methanes in Table XLI are guided by a comparison with the calculated values obtained by Johnston and Dennison[6] from the equations of Rosenthal with the constants in (126). The calculated values in the above table are, however, those obtained by Benedict who took into account the anharmonic corrections.[2] It is seen that the agreement between the observed and the calculated values is satisfactory.

Assignment	Obs. ν	Obs. $\Delta\nu$	Calc. $\Delta\nu$
ν_1	2983.0 $\parallel$		
$\nu_2(2)$	1477.1 $\perp$	5 – 6	5.2
ν_{3b}	2205.25 $\parallel$	7.714	
$\nu_{3ab}(2)$	3031.0 $\perp$		2.3
ν_{4a}	1306.8 $\parallel$	7.7	
$\nu_{4ab}(2)$	1155.3 $\perp$	3.8–4.5	3.3
$2\nu_2$	2923		

Table XLII. Infrared spectrum of CH_3D

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[6] M. Johnston & D. M. Dennison, Phys. Rev. 47, 94, (1935).

Table XLII gives the results of Ginsberg and Barker. The 2983, 3031 and 2923 cm^{-1} bands are not resolved into rotational lines on account of the overlapping with one another. The band at 2205 cm^{-1} is however completely resolved and from the spacing $\Delta\nu=7.714\ \mathrm{cm}^{-1}$, it is possible to obtain the moment of inertia I_A

$$I_A = 7.166 \times 10^{-40}\ \mathrm{g.cm}^2 \tag{128a}$$

and on the assumption of a regular tetrahedral model,

$$I_C = 5.298 \times 10^{-40}\ \mathrm{g.cm}^2, \qquad r\,(\mathrm{C-H}) = 1.093\ \mathrm{\AA}. \tag{128b}$$

With these dimensions and the constants in (126), Johnston and Dennison obtained for the internal angular momenta for the 3 degenerate vibrations

$$\xi_2 = -\ 0.25, \qquad \xi_{3ab} = 0.03, \qquad \xi_{4ab} = 0.59. \tag{129}$$

The spacings calculated according to Table IV of Chap. IV are given in Table XLII. It is seen that the agreement with the observed values is satisfactory in the case of the 1477 and 1156 cm^{-1} bands.

The results of Nielsen's on CD_4 are given in Table XLIII. From the spacings in the ν_3 and ν_4 bands and Table IV, one obtains

$$I = 10.44 \times 10^{-40}\ \mathrm{g.cm}^2. \tag{130}$$

From (98) and Table IV of Chap. IV, one obtains $\xi_3=0.1465$ and $\xi_4=0.3535$ and the spacing for the $\nu_3+\nu_4$ band. Nielsen and Nielsen suggested that the poor agreement between the calculated and the observed for the 2992.8 cm^{-1} band may be due to its being the 3000 cm^{-1} band of CHD_3. Further work on the harmonic and combination bands of the molecule is desirable.

Assignment	Obs. ν	Obs. $\Delta\nu$	Calc. $\Delta\nu$
ν_1	2085 Ra.		
$\nu_2(2)$	?		
$\nu_3(3)$	2259	4.53	*
$\nu_4(3)$	995.86	3.42	*
$\nu_1+\nu_4$?	2992.8	7.11	3.42
$\nu_3+\nu_4$	3103.7	5.01	6.62

Table XLIII. Infrared spectrum of CD_4

Finally, it is worth noticing that in the Raman spectra of the deutero-methanes, quite a number of harmonic frequencies appear (see Table XLI, and also the 3072 cm^{-1} line in CH_4 in Table XL). Some of these appear probably as the result of the resonance interaction between one intense fundamental and a harmonic of a second fundamental, similar to the situation in CO_2 and CS_2 discussed in Chap. III, §4, B. The non-appearance of the active fundamental ν_2 in CH_4 and CD_2 may be due to the smallness of the change of the polarizability, and hence the induced electric moment, in these vibrations.

2) SiH_4

The infrared spectrum of silane SiH_4 has been studied by Steward and Nielsen,[1] and the Raman spectrum by Stitt and Yost.[2] The observed bands and their assignments are given in Table XLIV.

Assignment	Obs. ν	Obs.$\Delta\nu$	Calc.$\Delta\nu$
ν_1	2187 Ra.		
$\nu_2(2)$	978 Ra.		
$\nu_3(3)$	2183	5.65	*
$\nu_4(3)$	919	3.5	*
$\nu_2+\nu_4$	1900		3.5
$\nu_3-\nu_4$	1260		
?	1680		
$\nu_3+\nu_4$	3095	9.7	7.7
$\nu_2+\nu_3$	3153	4.7	5.65
$2\nu_3$	4360		3.5

Table XLIV. Vibrational spectrum of SiH_4

From the observed spacings in the ν_3 and ν_1 bands and by means of Table IV, Chap. IV, one obtains the following dimensions

$$I = 8.9\times10^{-40}\text{g.cm}^2, \quad r\,(Si-H) = 1.54\,\text{Å}, \quad r\,(H-H)=2.31\,\text{Å}. \qquad (131)$$

These values must be regarded as approximate since the value of I is quite sensitive to the spacings $\Delta\nu_3$ and $\Delta\nu_4$. Comparison of the Si−H distance with the value 1.53 Å for the normal electronic state of the diatomic molecule SiH (frequency=2012 cm^{-1}) shows, however, that the values in (131) are probably correct in their order of magnitude.[3]

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[1] W. B. Steward & H. H. Nielsen, Phys. Rev. 47, 828, (1935).

[2] F. B. Stitt & D. M. Yost, Jour. Chem. Phys. 4, 82, (1936).

[3] Cf. H. Sponer, *Molekülspektren* I, P. 26, (1935); G. D. Rochester, Zeits. f. Physik 101, 796, (1936), gave r_0=1.51A, ω =2080 cm^{-1}.

By means of (87), Chap. IV, one obtains $\xi_3=0.08$, $\xi_4=0.42$. From (125), one obtains $\delta_3=0.21$ and $\delta_4=0.53$ and hence the following values for the constants in (108),[4]

$$A=4.15, \quad B=0.262, \quad C=0.0875, \quad D=1.16, \quad E=0.186. \qquad (132)$$

From (114), the constants in the valence plus central force potential (111) can be calculated,

$$k_{SiH} = 2.90, \quad k_\alpha = 0.22, \quad k_{HH} = 0.015, \quad k_2 = 0.084, \qquad (133)$$

3) GeH_4

The infrared spectrum of GeH_4 has been studied by Steward and Nielsen,[1] but no Raman data seem to have been reported. The observed bands and their assignments are given in Table XLV.

Assignment	Obs. ν	Obs. $\Delta\nu$
ν_1	(1988.7)	
$\nu_2(2)$	(820)	
$\nu_3(3)$	2110.1	5.56
$\nu_4(3)$	934	6 uncertain
$2\nu_4$?	1666	
$\nu_2+\nu_4$	1754	
$\nu_1+\nu_4$	2922.7	
$\nu_3+\nu_4$	3031.0	6.2
$2\nu_3$	4250	

Table XLV. Infrared spectrum of GeH_4

The values for ν_1 and ν_2 are the assumed values to account for the other bands. Because of the uncertainties in the frequencies ν_1 and ν_2, and especially in the spacing $\Delta\nu$ in the fundamental ν_4, it seems premature to attempt any calculation of the dimensions and the potential function of the molecule.[2] The complexity of the ν_4 band is undoubtedly due to the Coriolis interaction between ν_4 and ν_2 as suggested by Jahn and Childs.[3]

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[4] Here the positive value of the constant D has been used by analogy with the case of CH_4. Application of the relations (119) shows that the simple valence force potential is a good approximation, the two sides of both equations differing by 6-7 %.

[1] W. B. Steward & H. H. Nielsen, Phys. Rev. 47, 792; 48, 861, (1935).

4) CF_4, 5) SiF_4

The Raman spectra of these molecules have been studied by Yost, Lassettre and Gross[1] and the infrared spectra more recently by Bailey, Hale and Thompson.[2] The observed frequencies and their assignments are summarized in Table XLVI.

Assignment	CF_4			SiF_4		
	Obs.ν		Calc.ν	Obs.ν		Calc.ν
ν_1	904	Ra.	*	800	Ra.	*
$\nu_2(2)$	437	Ra.	*	(268)		*
$\nu_3(3)$	1265		*	1022		*
$\nu_4(3)$	630	(635 Ra.)	*	(463)		*
$\nu_2+\nu_4$	1112	s	1067	645		680
$\nu_3-\nu_2$			828	775		762
$2\nu_4$	1250		1262	838	m	840
$2\nu_2+\nu_4$	1516		1504	912		940
$\nu_1+\nu_4$	1553	m	1534	1202	s	1220
$\nu_2+\nu_3$	1696		1702	1287	m	1282
$\nu_3+\nu_4$	1904		1895	1447		1442
$\nu_1+\nu_3$	2179		2169	1822	m	1822
$2\nu_3$	2541		2530	2051	m	2044
$\nu_2+2\nu_3$			2967	2332	m	2304
	906	impurity ?				

Table XLVI. Vibrational spectra of CF_4 and SiF_4.
Infrared bands marked s are strong, m medium, and those unmarked are weak.

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[2] From the $\Delta\nu$'s in the ν_3 and ν_4 bands, Steward and Nielsen obtained the following dimensions for the molecule:

$$I=7.0\times10^{-40}\ \text{g.cm}^2, \qquad r(\text{Ge}-\text{H})=1.27\text{Å}, \qquad r(\text{H}-\text{H})=2.06\text{Å}$$

(The value given for $r(\text{Ge}-\text{H})$, namely, 1.37Å, seems to be a misprint). But the low values of I and $r(\text{Ge}-\text{H})$ seem unreasonable on comparison with the corresponding values in CH_4 and SiH_4. This is to be traced to the uncertainty in the value of $\Delta\nu_4$. Assuming their calculation to be correct, then one finds

$$A=4.83, \quad B=0.23, \quad C=0.10, \quad D=\pm0.70, \quad E=0.146$$
$$k_{GeH}=3.12, \quad k_\alpha=0.84, \quad k_{HH}=-0.195, \quad k_2=0.042.$$

[3] H. A. Jahn & W. H. J. Childs, Nature 141, 916, (1938).

[1] D. M. Yost, E. N. Lassettre & S. T. Gross, Jour. Chem. Phys. 4, 325, (1936).

[2] Bailey, Hale, Thompson, Proc. Roy. Soc. A 167, 555, (1938); also Eucken & Bertram, Zeits. f. phys. Chem. B 31, 361, (1936).

The fundamental ν_2 of SiF_4 has not been observed in the Raman spectrum, and ν_4 lies outside the range covered in the work of Bailey, *et al.* The values in the table are the estimated values so as to give a satisfactory assignment to the other infrared bands.

For the potential of these molecules, application of the relations (119) shows that the simple valence force potential is entirely inadequate. These authors show that a central force potential gives better results, but the potential (120) of Urey and Bradley is most satisfactory. The values of the constants in (117) and (122) that give the best fit with the observed frequencies in Table XLVI are shown in Table XLVII.

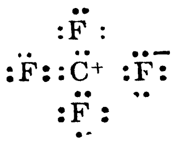
	Central force			Urey-Bradley potential	
	CF_4	SiF_4		CF_4	SiF_4
$k_{Y\text{-}F}$	3.08	4.95	$k_{Y\text{-}F}$	3.99	5.60
k_{FF}	1.51	0.55	k_{FF}	0.67	0.57
k_2	−0.51	−0.84	k'	0.73	0.25

Table XLVII. Potential constants of CF_4 and SiF_4[3]

The C−F and Si−F distances in these molecules are known from electron diffraction measurements,[4]

$$r\,(C-F) = 1.36\ \text{Å} \qquad r\,(Si-F) = 1.54\text{Å}$$

That these distances are smaller than the values calculated from the sums of the radii of the respective atoms according to Pauling,[5] viz., $r(C-F) = 1.41$ Å, $r(Si-F) = 1.81$ Å, was suggested by Pauling[6] *et al* as indicating some possible double bond contributions from resonance with such structure as



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[3] The constants in the potential (111) are given in Table XLVIII.

[4] Cf. L. O. Brockway, Rev. Mod. Phys. 8, 231, (1936).

[5] L. Pauling & Brockway, Jour. Am. Chem. Soc. 59, 1223, (1937).

[6] L. Pauling, quoted by H. O. Jenkins & L. O. Brockway, Jour. Am. Chem. Soc. 58, 2036, (1936).

Any conclusion, however, must depend for its validity on the accuracy of the electron diffraction data.[7]

6) CCl_4, 7) $SiCl_4$, 8) $TiCl_4$, 9) $SnCl_4$, 10) CBr_4, 11) $SiBr_4$, 12) $GeBr_4$, 13) $SnBr_4$, 14) SO_4, 15) PO_4, 16) ClO_4, 17) IO_4, 18) WO_4

The Raman spectra of these molecules and ions have been studied by a number of authors.[1] The observed frequencies are summarized in Table XLVIII.

	ν_1	ν_2	ν_3	ν_4	$k_{Y\text{-}X}$	k_α	k_{XX}	k_2
CF_4	904	437	1265	630	5.40	0.41	0.63	−0.023
SiF_4	800	(260)	1022	(420)	5.50	0.03	0.42	−0.24
CCl_4	460 0.05	214 0.83	790 0.86	311 0.79	1.89	0.07	0.63	−0.09
$SiCl_4$	422 0.05	149 0.86	608 0.86	220 0.86	2.57	0.04	0.28	−0.06
$TiCl_4$	386 0.05	119 0.86	491 0.86	139 0.86	2.41	0.04	0.16	−0.022
$SnCl_4$	367 0.05	104 0.86	401 0.65	136 0.86	2.29	0.02	0.12	−0.035
CBr_4	265	125	667	183	1.38	0.06	0.48	−0.08
$SiBr_4$	249	90	487	137	1.74	0	0.24	−0.097
$GeBr_4$	234	78	328	111				
$SnBr_4$	220	64	279	88	1.85	0.02	0.11	−0.022
$SO_4^=$	980	451	1113	620	6.05	0.28	0.755	−0.33
$PO_4^{\equiv}$	989	358	1061	518	5.62	0.03	0.89	−0.224
ClO_4^-	935	467	1121	634	6.24	1.51	0.50	−0.426
IO_4^-	800		841	702				
WO_4	880	216	932	356	7.35	−0.01	−0.027	−0.486

Table XLVIII. Fundamental frequencies and potential constants of tetrahedral molecules and ions.

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[7] Bailey, Hale & Thompson, *loc. cit.* These authors also calculated the bond distances from the bond constants by means of the Badger relation. In polyatomic molecules, such calculations are subject to this serious uncertainty, namely, there is always some ambiguity inherent in the bond constant since its value depends on the form of the potential chosen, as seen in Tables XLVII, and XLVIII. No such ambiguity arises in the case of diatomic molecules.

[1] Cf. Kohlrausch, *Der Smekal-Raman Effekt*, P. 215 and P. 218; polarization data from Cabannes & Rousset, Ann. de Physique 19, 229, (1933); $GeBr_4$ from Tchakirian and Volkringer, C. R. 200, 1758, (1935).

From the four fundamental frequencies in each of the molecules and ions in Table XLVIII, it is possible to calculate the constants in the potential (111). These constants are given in the last four columns in the table.[2] It may be emphasized that none of these molecules and ions can be satisfactorily represented by the simple valence force potential.

The Raman spectrum of CCl_4 has been studied in detail by Langseth[3] who found that the $\nu_1=458$ cm^{-1} line has a fine structure showing 3 components separated by 3.1 and 3.2 cm^{-1}, the $\nu_2=217$ line is a doublet with a spacing of 2.2 cm^{-1}, the ν_3 line is a doublet with one component at 762 and one at 790 cm^{-1}, each component being unresolved, and the $\nu_4=311$ line is also a doublet with a spacing of 2.9 cm^{-1}. The explanation of the 2 lines at 762 and 790 is that they arise from the resonance interaction between ν_3 and $\nu_1+\nu_4$. Langseth suggested that the fine structure in the other lines is in part due to the Cl isotope effect, namely, to the molecules CCl^{35}_4, $CCl^{35}_3Cl^{37}$, $CCl^{35}_2Cl^{37}_2$, $CCl^{35}Cl^{37}_3$, CCl^{37}_4 which are present in the ratio 31.6:42.2:21.1:4.7:0.4 according to the abundance ratio of the two Cl isotopes. The last 2 species of molecules are relatively rare so that their Raman lines are probably too weak to be observed. On the basis of a rough calculation of the isotope shifts for the first 3 species, Langseth found that they do not agree with the observed shifts and suggested that the fine structure in the ν_2 and ν_4 lines may be due to a deviation of the molecule from tetrahedral symmetry. More recently, from the equations of Rosenthal for the isotope shifts in YX_4 molecules,[5] Wu and Sutherland[4] have shown that the observed fine structure of all the Raman lines is compatible with the assumption that it is entirely of isotopic origin. It is not yet possible, however, to decide the form of the potential, *i.e.*, whether the potential is that of Rosenthal or that of Urey and Bradley, from the present data. For this purpose, it is necessary to re-examine the Raman lines under high resolving power and high dispersion.

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[2] From (116), one obtains 2 values for the constant D, and for each value a set of values of A and B is obtained. Of the 4 sets of constants, the one leading to what is considered reasonable values is given in the table. See Rosenthal, Phys. Rev. 46, 730, (1934).

[3] A. Langseth, Zeits. f. Physik 72, 350, (1931).

[4] C. K. Wu & G. B. B. M. Sutherland, Jour. Chem. Phys. 6, 114, (1938).

[5] The potential is the most general one consistent with the tetrahedral symmetry of the molecule. See (108) and references given there. To determine the 5 potential constants from only 4 frequencies, recourse is made to the relations between these constants and those in the molecule ZYX_3 such as $CHCl_3$, obtained by H. H. Voge and J. E. Rosenthal, Jour. Chem. Phys. 4, 137, (1936).

C) Axially Symmetrical ZYX_3 Molecules

When one of the X atoms in a tetrahedrally symmetrical molecule YX_4 is replaced by a different atom Z (or by an isotope of X), the symmetry class of the molecule becomes C_{3v}, the elements of symmetry being a 3-fold axis of symmetry and 3 planes of symmetry containing it. There are 3 vibrations which are symmetrical with respect to the axis and are called the parallel vibrations. There are 3 vibrations which involve motions of the Y and Z atoms in directions perpendicular to the symmetry axis. Each of these perpendicular vibrations is doubly degenerate since the motions of the Y and Z atoms are isotropic in these directions. The nature of these vibrations and the order of magnitude of their frequencies can be roughly described and estimated as follows: If the interaction between the Z and the X atoms is small compared with their interactions with the Y atom, then one of the 3 parallel vibrations is approximately the valence vibration ν_1 in the YX_3 group, one the deformation vibration ν_3 in the YX_3 group, and one the Y–Z vibration. Of the 3 perpendicular vibrations, one is the valence vibration ν_2 in the YX_3 group, one the deformation vibration ν_4 in YX_3, and the last a vibration of the Y atom with respect to the rest of the molecule perpendicular to the symmetry axis. They are shown in Fig. 32. (see Fig. 26 for the vibrations of YX_3).

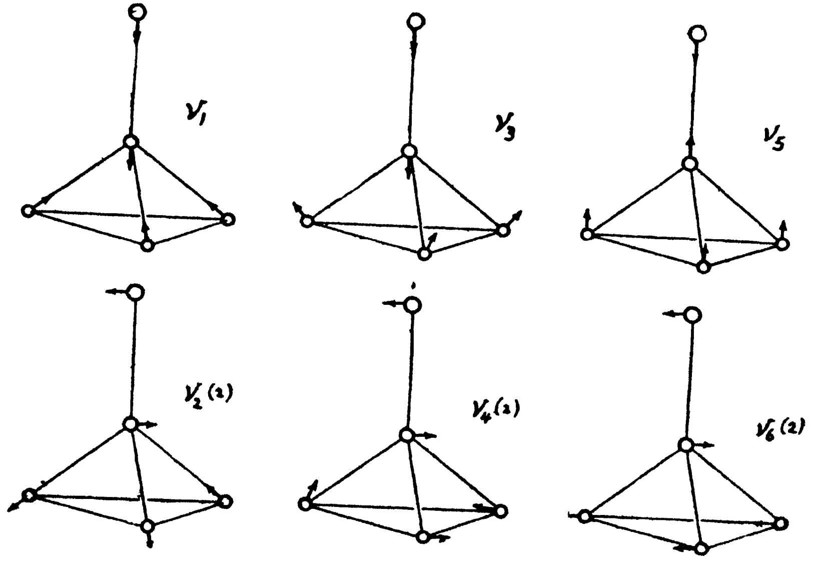

Fig. 32. Normal vibrations of axially symmetrical ZYX_3 molecules

The selection rules for the fundamental vibrations are as follows: The parallel vibrations gives rise to vibration-rotational bands of the parallel type discussed in §2, Chap. IV, and their Raman lines are polarized ($\varrho<6/7$). The perpendicular vibrations give rise to the perpendicular type bands and their Raman lines are depolarized ($\varrho=6/7$).

The problem of the normal vibrations of a ZYX_3 molecule has been treated by a number of authors. Rosenthal and Voge showed that the most general potential function demanded by the symmetry of the molecule contains 12 constants, 6 for that part of the potential for the parallel and 6 for the perpendicular vibrations.[1] While such a potential is free from simplifying assumptions, it has the disadvantage that the 12 constants in general cannot be uniquely determined from the observed frequencies. These authors have shown, however, that certain of the constants remain practically unchanged in passing from the molecule ZYX_3, to TYX_3 or YX_4, and certain relations can be obtained connecting the potential constants in the different molecules possessing certain identical groups. We shall rather refer to their papers for these somewhat lengthy expressions.

For practical purpose, potential functions which contain a fewer number of constants and hence are less general have been proposed. The treatment of the parallel vibrations is particularly simple. One simple potential is the following

$$2V = a\,x^2 + b\,q^2 + c\,x_0^2 + 2d\,q\,x + 2e\,x\,x_0,\tag{134}$$[2]

where x_0 is the change in the Z−Y distance, x the change in the distance from the Y atom to the c. g. of the X atoms, and q the displacement of each X atoms perpendicular to the symmetry axis. The determinantal equation gives

$$\lambda_1+\lambda_3+\lambda_5=\frac{M+3m}{3mM}\,a+\frac{b}{3m}+\frac{M+M_1}{MM_1}\,c-\frac{2}{M}\,e,$$

$$\lambda_1\lambda_3+\lambda_3\lambda_5+\lambda_5\lambda_1=\frac{M+M_1+3m}{3mMM_1}\,(ac-e^2)+\frac{M+M_1}{3mMM_1}\,bc+\frac{M+3m}{9m^2M}\,(ab-d^2),$$

$$\lambda_1\lambda_3\lambda_5=\frac{M+M_1+3m}{9m^2MM_1}\Big[(ab-d^2)\,c-be^2\Big],\tag{135}$$

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[1] J. E. Rosenthal & H. H. Voge, Jour. Chem. Phys. 4, 134, (1936); Voge & Rosenthal, *ibid.*, 4, 137, (1936).

[2] G. B. B. M. Sutherland & D. M. Dennison, Proc. Roy. Soc. A 148, 250, (1935), introduced the potential (134) with $e=0$. The interaction between the Z and the X atoms is then completely neglected.

where M_1, M, m are the masses of the Z, Y, X atoms respectively.

Another potential that proves useful (for the methyl halides in particular) is the modified valence potential

$$2V=3k\,(\delta r)^2+k_1\,(\delta r)^2+3k_\theta\,(r\delta\theta)^2+3k_\varphi\,(s\delta\varphi)^2+6k_4\,(s\delta\varphi)\,\delta r_1, \qquad (136)$$

where δr, δr_1 are the changes in the Y−X and the Z−Y bond distances respectively, and θ, φ the changes in the bond angles $\widehat{XYX}$ and $\widehat{ZYX}$ respectively. The angles θ and φ are not independent. It can be shown that (136) can be put in the form[3]

$$2V = 3k\,(\delta r)^2 + k_1\,(\delta r_1)^2 + 3k_\alpha\,(s\delta\varphi)^2 + 6k_4\,(s\delta\varphi)\,\delta r_1, \qquad (136a)$$

where

$$k_\alpha s^2 = k_\varphi s^2 + k_\theta r^2 \;\frac{12\cos^2\varphi}{(1+3\cos^2\varphi)} \qquad (137)$$

The kinetic energy for the parallel vibrations is

$$2TS=3m(M_1+M+3m\sin^2\varphi)\,\dot{r}^2+3m(M_1+M+3m\cos^2\varphi)r^2\dot{\varphi}^2+M_1(M+3m)\dot{r}_1^2$$
$$-\,18\,m^2\cos\varphi\sin\varphi\; r\,\dot{r}\,\dot{\varphi}\;+6mM_1\,(\dot{r}\cos\varphi\;+\;r\,\dot{\varphi}\sin\varphi)\;\dot{r}_1$$

where $S=M+M_1+3m$. The determinantal equation gives

$$\lambda_1+\lambda_3+\lambda_5=\frac{M+M_1}{MM_1}k_1+\left(\frac{1}{m}+\frac{3}{M}\cos^2\varphi\right)k+\left(\frac{1}{m}+\frac{3}{M}\sin^2\varphi\right)k_\alpha\left(\frac{s}{r}\right)^2$$
$$-\frac{6}{M}\sin\varphi\;k_4\left(\frac{s}{r}\right),$$

$$\lambda_1\lambda_3+\lambda_3\lambda_5+\lambda_5\lambda_1=\frac{M_1+M+3m\sin^2\varphi}{mMM_1}\left[k_1k_\alpha-3k_4^2\right]\left(\frac{s}{r}\right)^2+\left[\frac{M+3m}{m^2M}\;k_\alpha\left(\frac{s}{r}\right)^2\right.$$
$$\left.+\frac{M_1+M+3m\cos^2\varphi}{mMM_1}k_1\right]k\;-\;\frac{6}{mM}\sin\;\varphi\;kk_4\left(\frac{s}{r}\right)$$

$$\lambda_1\lambda_3\lambda_5=\frac{S}{m^2MM_1}\left[k_1\,k_\alpha\left(\frac{s}{r}\right)^2-3k_4^2\left(\frac{s}{r}\right)^2\right]k \qquad (138)$$

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[3] Recently in an **abstract**, Z. I. Slawsky & D. M. Dennison, Phys. Rev. 53, 930, (1938), proposed such a potential, but their results do not seem to have appeared in full. The equations for the doubly degenerate frequencies are more complicated. They have recently been given by J. Wagner, Zeits. f. phys. Chem. B 40, 36, (1938).

For bands involving the harmonics or combinations of the perpendicular fundamentals, the same remark concerning the splitting of the band into a number of component bands given in the discussion on NH_3 holds here, (see footnote 10 in §2, B, 2).

1) CH_3F, 2) CH_3Cl, 3) CH_3Br, 4) CH_3I

The infrared spectra of the methyl halides have been studied by Bennett and Meyer,[1] Nielsen and Barker[2] and Plyler.[3] The Raman spectra have also been studied by a number of workers.[4] The experimental data are summarized in Table IL.

	CH_3F		CH_3Cl		CH_3Br		CH_3I	
	Infra.	Raman	Infra.	Raman	Infra.	Raman	Infra.	Raman
ν_1	2862 $\parallel$		2879 $\parallel$	2815	2861 $\parallel$		2855 $\parallel$	2889
$2\nu_4$	2965 $\parallel$		2967 $\parallel$	2955 (0.05)	2973 $\parallel$	2956 (0.10)	2971 $\parallel$	2947 (0.05)
$\nu_2(2)$	2987 $\perp$ 7.5		3047 $\perp$ 8.2	3024 (0.86)	3061 $\perp$ 9.0	3050 (0.86)	3074 $\perp$ 9.0	3046 (0.86)
ν_3	1476 $\parallel$	1462	1355 $\parallel$	1357 p	1306 $\parallel$	1296 p	1252 $\parallel$	1239 p
$\nu_4(2)$	1476 $\perp$ 11.5		1460 $\perp$ 12	1450 d	1450 $\perp$ 11.9	1420 d	1445 $\perp$ 11.8	1416 d
ν_5	1049 $\parallel$		732 $\parallel$	712 (0.15)	610 $\parallel$	594 (0.20)	532 $\parallel$	522 (0.25)
$\nu_6(2)$	1200 $\perp$ 5.65		1020 $\perp$ 6.95	1098 p	957 $\perp$ 7.42		885 $\perp$ 7.70	

Table IL. Infrared & Raman spectra of methyl halides.

Numbers in parentheses are the degrees of depolarization according to Cabannes and Rousset,[4] and the numbers under the infrared frequencies are the separations of the *Q* branches according to Bennett & Meyer.

It is seen that the frequencies ν_1, ν_2, ν_3, ν_4 change only a little in passing from CH_3F to CH_3I, but ν_5 and ν_6 decrease regularly down the series of molecules, in accordance with the approximate considerations given at the beginning of this section.

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[1] W. H. Bennett & C. F. Meyer, Phys. Rev. 32, 888, (1928).

[2] A. H. Nielsen & E. F. Barker, *ibid.*, 46, 970, (1934), CH_3Cl.

[3] E. F. Barker & E. K. Plyler, Jour. Chem. Phys. 3, 367, (1935), low frequency fundamentals of CH_3Br and CH_3I.

[4] Cf. Kohlrausch, *Der Smekal-Raman Effekt;* polarization measurements from J. Cabannes & A. Rousset, Ann. de Physique 19, 229, (1933).

From the observed spacings in the 3 ⊥ bands of each molecule in Table IL and by means of (98) and Table IV of Chap. IV, it is possible to calculate 4 of the quantities ξ_2, ξ_4. ξ_6. I_A, I_C if one of them is known. Assuming that the methyl group CH_8 retains the bone length and tetrahedral angle of CH_4 in these molecules, and taking the electron diffraction data for the carbon halogen distances,[5] one can calculate the moment of inertia I_A. I_C can then be calculated from Table IV as a check. The results of these calculation are given in Table L.[6]

	CH_8F	CH_8Cl	CH_8Br	CH_8I
C−X in Å	1.42	1.77 (7)	1.91	2.14
I_A in 10^{-40}	34.2	62.6	86.3	110
I_C from(85)	5.47	5.47	5.42	5.46
ξ_2	0.102	0.100	0.054	0.059
ξ_4	−0.294	−0.275	−0.235	−0.222
ξ_6	0.285	0.223	0.210	0.188

Table L. Molecular constants of methyl halides

[5] The electron diffraction data are from the following sources: CH_3F, L. O. Brockway, Jour. Phys. Chem. 41, 185, (1937); CH_3Cl, Brockway, Rev. Mod. Phys. 8, 231, (1936); CH_3Br, H. Lévy & Brockway, Jour. Am. Chem. Soc. 59, 1662, (1937) C−I from CI_4, C. Finbak & O. Hassel, Zeits. f. phys. Chem. B 36, 301, (1937).

[6] Johnston and Dennison, Phys. Rev. 48, 868, (1935), calculated the I_C by making use of the values of I_A obtained by Gerhard & Dennison, Phys. Rev. 43, 197, (1933), from the separations between the intensity maxima in the P and R branches of the parallel bands. The I_A for CH_3F was obtained from the rotational spacing $\Delta\nu=1.688$ cm^{-1} in the $\nu_5=1049$ parallel band measured by Bennett & Meyer and was given as 39.5×10^{-40}. The I_A for the CH_3F, CH_3Cl, CH_8Br, CH_3I molecules are 39.5, 51.5, 89, 99×10^{-40} respectively. These lead to the value 5.61, 5.35, 5.43, 5.44 for the I_C in these molecules, and C−F=1.54, C−Cl=1.58, C−Br=1.96, C−I= 2.01 Å.

From the spacing $\Delta\nu=1.688$ cm^{-1} in the ν_5 band of CH_3F, one should get for I_A the value 32.8×10^{-40} instead of 39.5×10^{-40} as given by Gerhard and Dennison. In fact, with $I_A=32.8\times0^{-40}$ one obtains for the C−F distance the value 1.39 Å, in much better agreement with the electron diffraction value than the value 1.54 Å.

G. Sutherland, Trans. Faraday Soc. 34, 202, (1938), gave the following values C−F=1.385, C−Cl=1.66, C−Br=1.88, C−I=2.07 Å as the "spectroscopic" values.

[7] A. H. Nielsen and H. H. Nielsen, Phys. Rev. 56, 274, (1939), found the spacing $\Delta\nu$ for the 1355 cm^{-1} band of CH_3Cl to be 1.15 cm^{-1}. From this, one obtains $I_A=48.5\times10^{-40}$, and C−Cl=1.53 Å.

In Table LI are given the results of Nielsen and Barker on CH_3Cl.[8] The assignments of the 2461, 4384, 4478 and 6050 cm^{-1} bands are supported by the agreement between the observed spacings $\Delta\nu$ and those calculated according to (98) and Table IV of Chap. IV and the constants in Table L. On the other hand, it seems difficult to reconcile the observed spacings in the 4176, 5900 and 10000 cm^{-1} bands with the calculated values, according to the assignments of Nielsen and Barker. It is possible that this is due to the complexity of these bands as the result of overlappings by the component bands. Further work on these bands is desirable.

	Obs. ν &		Predicted	Spacing	
Assignment	banh	type	band type	obs.	calc.
ν_5	732.3	∥	∥		
ν_6	1019.9	⊥	⊥	6.95	*
ν_3	1353.3	∥	∥		
ν_4	1459.6	⊥	⊥	12.0	*
ν_1	2879	∥	∥, ⊥, ∥		
$2\nu_4$	2967	∥			
ν_2	3047.2	⊥	⊥	8.2	*
$\nu_4+\nu_6$	2461.8	⊥	∥, ⊥, ∥	9.7	8.74
$\nu_2+\nu_6$	3981	⊥			12.5
	4047.9	∥	∥, ⊥, ∥		
	4089.6	∥			
$\nu_3+\begin{cases}\nu_1\\2\nu_4\end{cases}$	4175.8	⊥	∥, ⊥, ∥	9.7	8.7
	4230.6	∥			
$\nu_2+\nu_3$	4383.3	⊥	⊥	8.4	8.2
$\nu_2+2\nu_5$	4478.5	⊥	⊥	8.6	8.2
?	5400	⊥			
$\nu_1+\nu_2$	5900	⊥	∥, ⊥, ⊥, ∥, ∥	9.0	3.7
$2\nu_2$	6050	∥, ⊥	∥, ⊥	12	11.3
$3\nu_1+\nu_4$	10000	⊥	⊥	6.7	12
?	13800	⊥			

Table LI. Infrared spectrum of CH_3Cl

A feature observed in the perpendicular bands of the methyl halides is that every third *Q* branch is enhanced. This results from the statistical weights of the rotational states as a consequence of the nuclear spin ½ of the hydrogen atom in the molecule.[7]

In addition to the bands in Tables IL and LI, Verleger and Naudé[8] have observed two perpendicular bands, one weaker than the other, at about 9000 cm^{-1} in each of the methyl halides. The spacings between the *Q* branches are the same for the two bands in each molecule, and are 7.6, 8.47, 9.35 and 9.61 cm^{-1} in CH_3F, CH_3Cl, CH_3Br and CH_3I respectively. They assigned these bands to $2\nu_2+\left\{\begin{matrix}\nu_1\\ 2\nu_4\end{matrix}\right.$. The spacings calculated from Table IV of Chap. IV and the constants in Table L are 12, 11.3, 11.1, and 11.7 cm^{-1} respectively. Hence it seems more reasonable to assign them to $2\nu_1+\nu_2$ and $3\nu_2$; for the spacings in these cases are 7.5, 8.2, 9.0 and 9.0 cm^{-1} respectively, in better agreement with the observed values.[8]

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[7] See D. M. Dennison, Rev. Mod. Phys. 3, 280, (1931).

The appearance of two bands at *ca.* 2860 and 2970 cm^{-1} in both the absorption and the Raman spectra of the methyl halides has been explained as the result of a resonance interaction between the levels ν_1 and $2\nu_4$, as discussed in § 4, B, Chap. III. Adel and Barker[9] have made a first-order perturbation calculation similar to that for the CO_2 molecule. If the resonance discrepancy $\nu_1-2\nu_4$ be represented by Δ, and the coupling between the vibrations ν_1 and ν_4 by a term $hb\,\sigma\varrho^2$ in the potential, where σ and ϱ are the dimensionless coordinates appropriate to the normal vibrations ν_1 and ν_4 respectively, then

	CH_3F	CH_3Cl	CH_3Br	CH_3I
$\Delta =$	-38	4	16	26
$\lvert b \rvert =$	66	62	78	80

The relative values of Δ and $|b|$ show that the resonance is quite close in these molecules.

To obtain the potentials of the methyl halides, let us choose (136) and in a first approximation neglect the term $k_4(s\delta\varphi)\delta r_1$.[10] On assuming that these molecules still retain the tetrahedral angle so that $\cos^2\varphi=1/9$, we obtain the following values:

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[8] H. Verleger, Zeits. f. Physik 98, 342, (1935); CH_3Cl, CH_3Br and CH_3I; S. M. Naudé & Verleger, Phys. Zeits. 38, 919,· (1937), CH_3F. Another reason for our assigning these bands to $2\nu_1+\nu_2$ and $3\nu_2$ instead of to $2\nu_2+\nu_1$ and $2\nu_2+2\nu_4$ is perhaps the following: If the bands are due to the resonating levels $2\nu_2+\nu_1$ and $2\nu_2+2\nu_4$, one would expect them to have comparable intensities as in the 3000 cm^{-1} region and to be separated by about the same distance, viz., *ca.* 100 cm^{-1}, as in the 3000 cm^{-1} region. The observed intensities of the two bands are, howerver, quite different, and the separations between them are only 15 to 50 cm^{-1} in the four molecule.

[9] A. Adel & E. F. Barker, Jour. Chem. Phys. 2, 627, (1934).

[10] This is perhaps justified since one expects k_4 to be small and since the refinement obtained by including it is doubtful because the anharmonicity correction for the frequencies (which is of the order of 5 % for the high frequency fundamental) is not known. See however Slawsky & Dennison, footnote (3).

	k_{CH}	$k_{C\text{-}X}$	$k_\alpha\left(\frac{s}{r}\right)^2$	$k_\Theta r^2$	$k_\varphi s^2$
CH_3F	4.96	5.78	0.98	0.61	0.60
CH_3Cl	4.94	3.46	0.97	0.61	0.46
CH_3Br	4.94	2.82	0.82	0.61	0.40
CH_3I	4.96	2.23	0.77	0.61	0.34

Table LII. Potential constants of methyl halides.
The last two columns in 10^{-11} dynes cm/radian, the others in 10^5 dynes/cm.

The values of $k_\varphi s^2$ are obtained from $k_\alpha (s/r)^2$ by means of (137) and by giving the assumed value 0.50×10^5 obtained in CH_4 to k_Θ. Sutherland and Dennison[2] have calculated the constants in (134) with $e=0$. The constant c which corresponds to k_{CX} in (136) has the following values in the four molecules: 5.76, 3.44, 2.85, and 2.26. It is seen that these agree quite well with the values in Table LIII.

5) $CHCl_3$, 5a) $CDCl_3$, 6) $CHBr_3$, 7) CHI_3, 8) $SiHCl_3$, 9) $OPCl_3$, 10) CCl_3F, 11) CCl_3Br, 12) CBr_3Cl, 13) $SiCl_3Br$

The Raman spectra of these molecules are known.[1] The following table summarizes the observed frequencies and their assignments based on considerations of their order of magnitude, intensities and in a few cases the polarization characters. For the modes of the vibrations, reference is made to Fig. 32.

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[1] $CHCl_3$, $CHBr_3$, $SiHCl_3$ from Kohlrausch, Der Smekal-Raman Effekt; $CDCl_3$, R. W. Wood & D. H. Rank, Phys. Rev. 48, 63, (1935); $OPCl_3$, J. Cabannes & A. Rousset, Ann. de Physique 19, 229, (1933); CCl_3F, G. Glockler & G. R. Leader, Jour. Chem. Phys. 7, 278, (1939); CCl_3Br, CBr_3Cl, J. Lecomte, H. Volkringer & A. Tchakrian, C. R. 204, 1927, (1937); Jour. de Phys. et Rad. 9, 105, (1938); $SiCl_3Br$, de Hemptinne, Wouters & Fayt, Bull. Sci. Acad. Roy. Belg. 19, 318, (1933); CHI_3 (infrared), Emschwiller & Lecomte, Jour. de Phys. et Rad. 8, 130, (1937); Barchewitz & Parodi, *ibid.* 10, 143, (1939); Polarization measurements from Cabannes & Rousset, *loc. cit.*; and L. Simons, Soc. Sci. Fenn. Comm. 6, 13, (1932).

	$\nu_1 \parallel$	$\nu_2 \perp$	$\nu_3 \parallel$	$\nu_4 \perp$	$\nu_5 \parallel$	$\nu_6 \perp$
$CHCl_3$	668.6 (0.06)	761.2 (0.86)	365.9 (0.20)	262.0 (0.86)	3018.9 (0.20)	1215 (0.86)
$CDCl_3$	650.8	737.6	366.5	262.0	2256	908.3
$CHBr_3$	539 (0.06)	655 (0.53)	222 (0.11)	154 (0.77)	3021 (0.24)	1144 (0.86)
CHI_3	416?	576		112?		1053
$SiHCl_3$	489	587	250	179	2258	799
$OPCl_3$	486 (0.05)	581 (0.86)	267 (0.64)	193 (0.83)	1290 (0.4)	337 (0.81)
CCl_3F	535	833	349	244	1067	397
CCl_3Br	418	765	289	187	710	243
CBr_3Cl	326	674	210	139	734	266
$SiCl_3Br$	362	410	183	123	325	201

Table LIII. Fundamental frequencies of ZYX_3 molecules. Numbers in parentheses are the degrees of depolarization.

In an approximate manner, one may regard the frequencies ν_1, ν_2, ν_3, ν_4 as determined to a great extent by the YX_3 group and the frequencies ν_5, ν_6, by the Z-Y group, although the strong coupling between the two "groups" will change the frequencies somewhat. This is rendered clear by a comparison of the frequencies ν_1, ν_2, ν_3, ν_4 in $CHCl_3$, $CDCl_3$, CCl_3F, CCl_3Br. Further discussions of these assignments and their relations to such molecules as CH_3Cl, CCl_2Br_2, etc. will be given in the following section.

For the potential functions of these molecules, the general potential of Rosenthal and Voge would have been the most desirable were it not for the large number of constants that can not be determined from the six frequencies.[2] The valence force potential can hardly be expected to be satisfactory for these molecules since an application of (119) to the data on CCl_4, CBr_4 shows that the valence force potential cannot be employed and it is very unlikely that it can be employed in the ZYX_3 molecules containing the CCl_3, CBr_3 groups. For the chloroforms $CHCl_3$ and $CDCl_3$, since there are altogether 6 parallel vibrations, the potential (134) with 5 constants can be used. Application of the third equation in (135) to these frequencies shows that the relation is not exactly satisfied. This is due to the fact that the frequencies, especially the C-H and C-D frequencies, in Table LIII have not been corrected for anharmonicity, the correction being greater for the C—H than for the C—D frequencies.

[2] Voge & Rosenthal, Jour. Chem. Phys. 4, 137, (1936), $CHCl_3$ and $CDCl_3$.

Hence we shall regard ν_5 of $CHCl_3$ as unknown and calculate it along with the potential constants in (134). The result is

$$a=1.89,\quad b=19.5,\quad c=5.0,\quad d=\pm 3.12,\quad e=-0.265,\quad \nu_5=3050 \qquad (139)$$

Similar calculations cannot be carried out for the other molecules.

D) Tetrahedral Z_2YX_2 Molecules

When 2 of the X atoms in a tetrahedral YX_4 molecule are replaced by 2 Z atoms (or 2 isotopes of X), the symmetry class of the resulting molecule becomes that of C_{2v}, the elements of symmetry being a 2-fold axis bisecting the 2 angles $\widehat{XYX}$ and $\widehat{ZYZ}$ and two planes of symmetry one containing the YX_2 and the other the YZ_2 group. The symmetry properties and the selection rules for the normal vibrations are given in Table LIV, and the general forms of the vibrations are shown in Fig. 33.

class	Symmetry Z-X	 Z-Y	 z-axis	No. of vibr's	Selection rules Infrared	 Raman
A_1	*s*	*s*	*s*	4	$\mathfrak{M}_z$	p
B_1	*s*	*a*	*a*	2	$\mathfrak{M}_x$	d
B_2	*a*	*s*	*a*	2	$\mathfrak{M}_y$	d
A_2	*a*	*a*	*s*	1	inactive	d

Table LIV. Symmetry properties of normal vibrations of Z_2YX_2 molecules & selection rules.

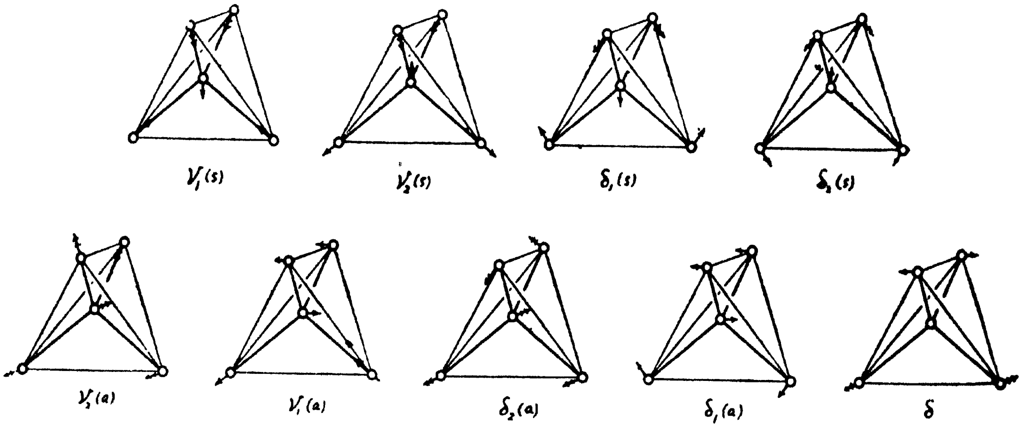

Fig. 33. Normal vibrations of tetrahedral Z_2YX_2 molecules. Single arrows represent displacements in the plane of paper; doubled arrows in a plane perpendicular to the plane of paper.

The normal vibrations of the Z_2YX_2 molecule have not been treated mathemtically in the literature probably because of the large number of potential constants necessary in such a molecule. But the order of magnitude of the normal frequencies can be estimated on the following qualitative considerations of the nature of the normal vibrations and their relations to the normal vibrations of the molecules YX_4, ZYX_3, Z_3YX and YZ_4. Of the 4 totally symmetrical vibrations, one is roughly the valence vibration ν_1 in the YX_2 group, one the same vibration ν_1 in YZ_2, one the deformation vibration ν_2 in YX_2, and one the same vibration ν_2 in YZ_2. Of the 2 vibrations in the symmetry class B_1, one is roughly the valence vibration ν_3 in YX_2, or more accurately, the vibration ν_4 of the molecule (2Z)-YX_2 in Fig. 29. The other is then the vibration ν_5 of (2Z)-YX_2. The two vibrations in the class B_2 are similarly the vibrations ν_4 and ν_5 of the molecule (2X)-YZ_2 in Fig. 29. The vibration in the class A_2 is a torsional oscillation of the two groups YX_2 and YZ_2 about the symmetry axis. These descriptions are also seen from Fig. 33.

The following diagram gives the relations among the normal vibrations of the series of molecules YX_4, ZYX_3, Z_2YX_2, Z_3YX and YZ_4. In fact this diagram has already been employed in correlating the frequencies of the deutero-methanes in Table XLI.

$$\begin{tikzcd}
YX_4 & \nu_1 \arrow[d, dash] & & & \nu_3(3) \arrow[dl, dash] \arrow[dr, dash] & & & \nu_2(2) \arrow[d, dash] & & & \nu_4(3) \arrow[dl, dash] \arrow[dr, dash] & & & \\
YX_3Z & \nu_1(\parallel) \arrow[d, dash] & & \nu_2(\perp) \arrow[dl, dash] \arrow[dr, dash] & & \nu_3(\parallel) \arrow[d, dash] & & \nu_4(\perp) \arrow[dl, dash] \arrow[dr, dash] & & \nu_5(\parallel) \arrow[d, dash] & & \nu_6(\perp) \arrow[dl, dash] \arrow[dr, dash] & & \\
YX_2Z_2 & \begin{matrix} A_1\nu_1(s) \\ [\nu_1] \end{matrix} \arrow[d, dash] & \begin{matrix} B_1\,\nu_1(a) \\ [\nu_{3a} \end{matrix} \arrow[dr, dash] & & \begin{matrix} B_2\,\nu_2(a) \\ \nu_{3c}] \end{matrix} \arrow[dl, dash] & \begin{matrix} A_1\nu_2(s) \\ [\nu_{3b}] \end{matrix} \arrow[d, dash] & \begin{matrix} A_2\delta \\ [\nu_{2a} \end{matrix} \arrow[dr, dash] & & \begin{matrix} A_1\delta_1(s) \\ \nu_{2b}] \end{matrix} \arrow[dl, dash] & \begin{matrix} A_1\,\delta_2(s) \\ [\nu_{1b}] \end{matrix} \arrow[d, dash] & \begin{matrix} B_1\,\delta_1(a) \\ [\nu_{4a} \end{matrix} \arrow[dr, dash] & & \begin{matrix} B_2\,\delta_2(a) \\ \nu_{4c}] \end{matrix} \arrow[dl, dash] & \\
YXZ_3 & \nu_1(\parallel) \arrow[d, dash] & & \nu_2(\perp) \arrow[dr, dash] & & \nu_3(\parallel) \arrow[dl, dash] & & \nu_4(\perp) \arrow[d, dash] & & \nu_5(\parallel) \arrow[dr, dash] & & \nu_6(\perp) \arrow[dl, dash] & & \\
YZ_4 & \nu_1 & & & \nu_3(3) & & & \nu_2(2) & & & \nu_4(3) & & & (140)
\end{tikzcd}$$

In the diagram, the notations for the vibrations are the conventional ones in the case of the YX_4 and YX_3Z molecules. For YX_2Z_2, the notations suggested are meant to describe the symmetry and the approximate nature of the vibrations. For comparison, are given in brackets the notations of Rosenthal which are less descriptive but show more clearly their relations with the vibrations of the YX_4, YX_3Z molecules.[1]

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[1] J. E. Rosenthal, Phys. Rev. 46, 730, (1934).

1) CH_2Cl_2

The Raman spectrum and the infrared spectrum of this molecule have been studied by a number of authors[1],[2]. The Raman spectrum consists of 9 lines of which 4 are polarized and 5 depolarized. That they are the fundamentals is consistent with the selection rules in Table LV. Recently Corin and Sutherland found in the absorption spectrum a band at 1266 cm^{-1} which is by far more intense than the other bands but does not appear in the Raman spectrum. They assigned it to one of the fundamentals and explained the Raman line 1149 cm^{-1} as the difference frequency 1425-284. This has, however, the difficulty that the 1149 line appears with an intensity comparable with that of the 1425 line. On considerations of the polarization characters of the lines and their relation with the fundamentals of CH_3Cl and $CHCl_3$ according to tne diagram (140), we give an assignment of the fundamentals and the observed infrared bands in Table LV. Corin and Sutherland's classification is also given for comparison.[3] Since the anharmonicity coefficients are not known, it is not possible to decide on one classification in preference to the other by comparing the observed and the calculated frequencies in the two cases. An examination of the infrared bands with high resolving power so as to obtain the band envelopes is desirable since the eight infrared active fundamentals should have different structures, namely, the *A*, *B*, *C* type bands of an asymmetrical rotator.

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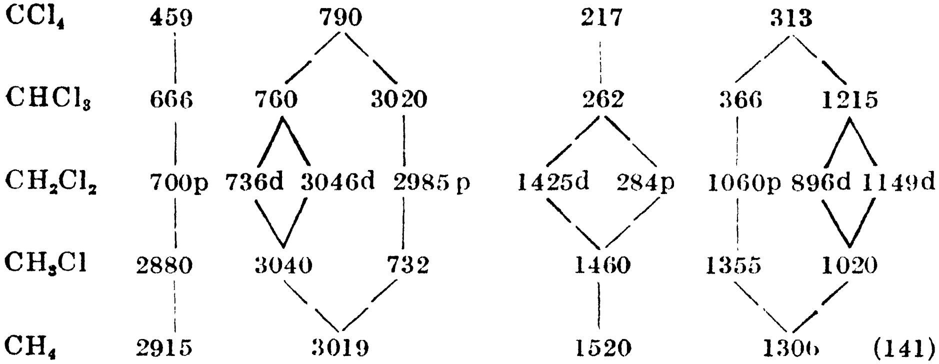
[1] Raman spectrum: J. Cabannes & A. Rousset, Ann. de Physique 19, 229, (1933); B. Trumpy, Zeits. f. Physik 88, 226, (1934); the polarization data of these authors agree (the 1425 cm^{-1} line is shown to be depolarized by Trumpy). Also Kohlrausch, Zeits. f. phys. Chem. B 29, 288, (1935).

[2] Infrared spectrum: C. Corin, Jour. Chim. Phys. 33, 448, (1936); J. Lecomte, C. R. 196, 1011, (1933); Emschwiller & Lecomte, Jour. de Phys. et Rad. 7, 130, (1937); Corin & Sutherland, Proc. Roy. Soc. A 165, 43, (1938).

[3] Corin and Sutherland, *loc. cit.*, considered the 2985, 1425, 3046 as the ν_1, ν_2, ν_8 of CH_2, 700, 284, 736 as the ν_1, ν_2, ν_3 of CCl_2, and the frequencies 896, 1060, 1266 as those of $(H_2)-C-(Cl_2)$. They estimated the frequencies of $\nu_{2a}, \nu_{4a}, \nu_{4c}$ in (140) by first regarding the CH_2Cl_2 as a hypothetical molecule $CH_2H_2^{35}$ and then as $CCl_2^{35}\,Cl_2^{1}$. While undoubtedly such a calculation is very useful in estimating the general region in which these frequencies would be found, it does not seem particularly helpful to discriminate between their assignments and those given in (141). Also the frequency for ν_{4a} of $CH_2^1\,H_2^5$ should be *ca.* 852 cm^{-1} instead of 1295 as given by them.



(141)

Obs. ν		ρ	I	Corin-Sutherland	Here suggested
284	Inf.	Ra(0.25)	(5)		$\delta_1(s)$
700	Inf.	Ra(0.07)	(15)		$\nu_1(s)$
736	Inf.	Ra(0.84)	(3b)		$\nu_1(a)$
896	Inf.	Ra(d)	(½b)		$\delta_1(a)$
1060	Inf.	Ra(p)	(1)		$\delta_2(s)$
1149	Inf.	Ra(0.87)	(2)	$\delta_2(a)-\delta_1(s)$	$\left\{\begin{array}{l}\delta\\ \delta_2(a)\end{array}\right.$ or $\left\{\begin{array}{l}\delta_2(a)\\ \delta\end{array}\right.$
1425	Inf.	Ra(0.83)	(3b)		
2985	Inf.	Ra(0.05)	(15)		$\nu_2(s)$
3046	Inf.	Ra(0.9)	(5b)		$\nu_2(a)$
985					$\delta_1(s)+\nu_1(s)$
1192	w				$\delta_1(s)+\delta_1(a)$
1222	w				$\nu_1(s)+2\delta_1(s)$?
1266	s			δ	$\nu_1(s)+2\delta_1(s)$
1548				$\delta+\delta_1(s)$	$\nu_1(s)+3\delta_1(s)$
1582	w				$\nu_1(s)+\delta_1(a)$
1613					$\nu_1(a)+\delta_1(a)$
1792	w				$2\delta_1(a)$; $\nu_1(a)+\delta_2(s)$
1984	w			$\delta+\nu_1(a)$	$\delta_2(s)+\delta_1(a)$
2058	w				$2\delta_1(a)+\delta_1(s)$
2137				$\delta+\delta_1(a)$	$\nu_1(s)+\delta_2(a)$;$2\nu_1(s)+\nu_1(a)$
2315					$\delta_1(a)+\delta_2(a)$
2415				$\delta+\delta_1(s)+\delta_1(a)$	$\nu_1(a)+\delta_1(s)+\delta_2(a)$
2525				2δ	$\delta_2(a)\delta$;$\nu_1(a)+2\delta_1(a)$
2674				$\delta+\delta_2(a)$	$\nu_1(a)+\delta_1(a)+\delta_2(s)$;$3\delta_1(a)$
3425	w				$\nu_1(a)+\nu_2(s)-\delta_1(s)$
3701					$\nu_1(a)+\nu_2(s)$
3937					$\delta_1(a)+\nu_2(a)$
4237				$\delta+\nu_2(s)$	$3\delta_2(a)$
4464					$\nu_2(a)+\delta_2(a)$

Table LV. Vibrational spectrum of CH_2Cl_2

In the assignment given in (141), the frequencies 284, 700, 736, 2985, 3046 cm^{-1} fall naturally into their places on considerations of both their polarization characters and their order of magnitude. The 1060 cm^{-1} line, which is polarized according to Trumpy, must then be $\delta_2(s)$, and 1425 cm^{-1} line which is depolarized must be either δ or $\delta_2(a)$.

Assuming $\delta=1425$ on consideration of the trend of the frequencies in passing from CCl_4 to CH_4, we are then left with two frequencies 1149 and 896 cm^{-1} and two vibrations $\delta_1(a)$ and $\delta_2(a)$. If these two Raman frequencies are fundamentals, then the reasonable assignment is $\delta_2(a)=1149$ and $\delta_1(a)=896$.[4] The rather large difference between the frequencies 1060, 1149 and those ordinarily ascribed to the deformation vibrations of the CH_2 group (*ca,* 1400 cm^{-1}) and also the difference between the frequencies 284 and 896 (which are ascribed to the deformation vibrations of CCl_2) can be explained as the result of the coupling between the CH_2 and the CCl_2 groups. This shows that in molecules like this, it is not strictly correct to speak of the "deformation vibrations" in the CH_2 or the CCl_2 group on account of the close coupling of the motions of the various atoms in the molecule.

2) CH_2F_2, 3) CH_2Br_2, 3a) CD_2Br_2, 4) CH_2I_2

The Raman and the infrared spectra of these molecules have been studied by a number of authors[1-3]. The observed frequencies are summarized in Table LVI and their assignments in (142), (143) and (144) in accordance with the diagram (140).

---

[4] P. Barchewitz & M. Parodi, Jour. de Phys. et Rad. 10, 143, (1939), assigned an infrared frequency 500 cm^{-1} to $\delta_2(s)$, and the 1240 cm^{-1} band of Emschwiller & Lecomte, *loc. cit.* (which is probably the 1266 cm^{-1} band of Corin & Sutherland) to $\delta_1(a)$, and 896 cm^{-1} to δ. That the 500 cm^{-1} band has no corresponding Raman line is an objection to its being a totally symmetrical frequency. The value 1266 cm^{-1} is a little too high for $\delta_1(a)$, since one would expect the mean of $\delta_1(a)$ and $\delta_2(a)$ to lie between the values 1020 cm^{-1} in CH_3Cl and 1215 cm^{-1} in $CHCl_3$.

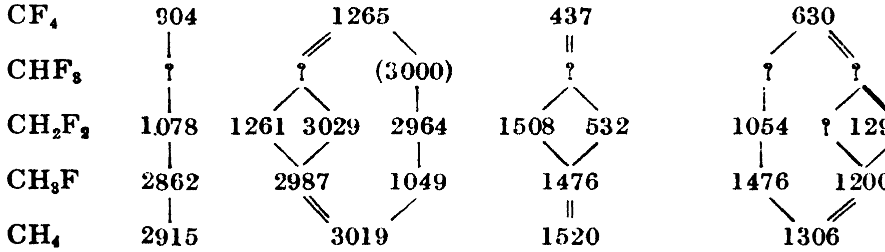
[1] CH_2F_2, Raman spectrum by Glockler & Leader, Jour. Chem. Phys. 7, 382, (1939).

[2] CH_2Br_2, Raman spectrum: Trumpy, Zeits. f. Physik 90, 133, (1934); 100, 250, (1936); Kohlrausch & Ypsilanti, Zeits. f. phys. Chem. B 29, 274, (1935); H. Gockel, *ibid.*, B 29, 79, (1935); Cabannes & Rousset, Ann. de Physique 19, 229, (1933); Emschwiller & Lecomte, Jour. de Phys. et Rad. 8, 130, (1937). Infrared: R. Titeica, Ann. de Physique 1, 533, (1934); Emschwiller & Lecomte, *loc. cit.*; Barchewitz & Parodi, Jour. de. Phys. et Rad. 10, 143, (1939).

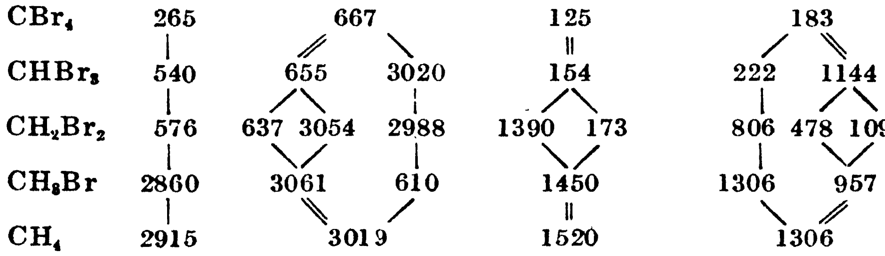
[3] CH_2I_2, Raman spectrum: Kohlrausch & Ypsilanti, *loc. cit.*; Emschwiller & Lecomte, *loc. cit.*; W. Bacher & J. Wagner, Zeits. f. phys. Chem. B 43, 191, (1939). Infrared: Titeica, *loc. cit.*; Emschwiller & Lecomte, *loc. cit.*; Barchewitz & Parodi, *loc. cit.*

CH_2F_2	CH_2Br_2		CD_2Br_2	CH_2I_2
ν	ν	ρ	ν	ν
532 (5)	173 (1b)	0.40	175	119 s
746 (0)	478 w			364
1079 (10)	578 * (20)	0.12	548	487 s
1261 (9)	638 * (4)	0.89	608	573 * s
1054 (3)	806 * w			713 * w
1294 (0)	1090 * w			1028 * w
1508 (3)	1390 * (1)	d	1023	1345 * s
2963 (10)	2988 (7)	0.10	2195	2970
3030 (5)	3054 (1)	0.85	2235	3091
	342 (2×173)			234 (2×119)
	1183 * (2×578) ?			963 (2×487)
	1267 (2×638; 173+1090)			1129 (119+1028)
2838 (4)				

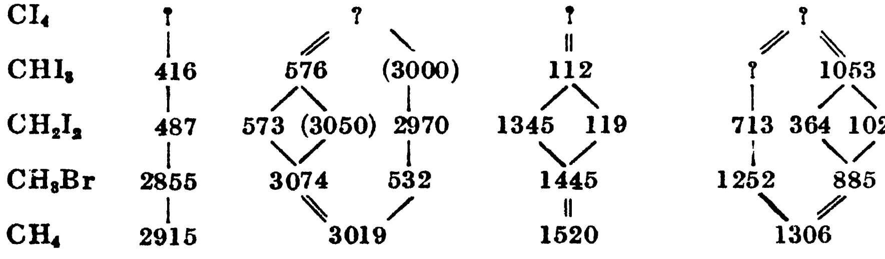
Table LVI. Raman spectra of CH_2F_2, CH_2Br_2, CD_2Br_2, CH_2I_2. Frequencies marked with * have also been observed in absorption.


CF₄ 904 1265 437 630
CHF₃ ? ? (3000) ? ? ?
CH₂F₂ 1078 1261 3029 2964 1508 532 1054 ? 1294
CH₃F 2862 2987 1049 1476 1476 1200
CH₄ 2915 3019 1520 1306

(142)


CBr₄ 265 667 125 183
CHBr₃ 540 655 3020 154 222 1144
CH₂Br₂ 576 637 3054 2988 1390 173 806 478 1090
CH₃Br 2860 3061 610 1450 1306 957
CH₄ 2915 3019 1520 1306

(143)


CI₄ ? ? ? ?
CHI₃ 416 576 (3000) 112 ? 1053
CH₂I₂ 487 573 (3050) 2970 1345 119 713 364 1028
CH₃Br 2855 3074 532 1445 1252 885
CH₄ 2915 3019 1520 1306

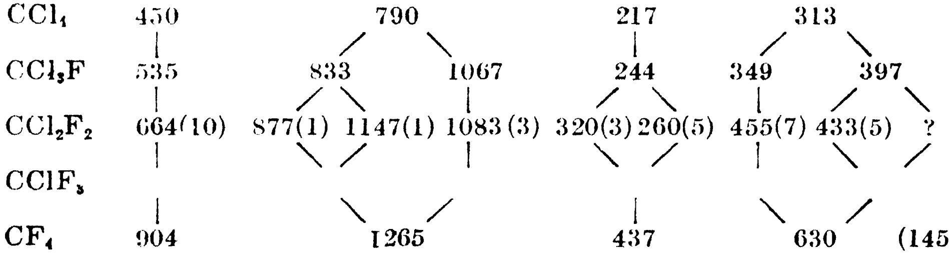
(144)

The assignment of the 6 Raman lines of CD_2Br_2 is shown in Table LVI in which the corresponding frequencies in CH_2Br_2 and CD_2Br_2 are given in the same line.

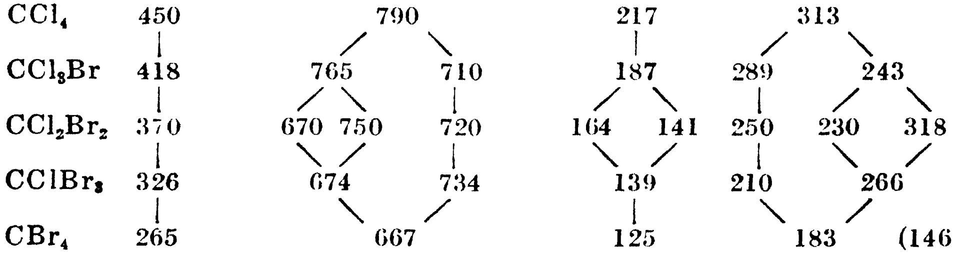
The assignments given in (142), (143) and (144) are guided mainly by considerations of the order of magnitude of the various frequencies, the trends in passing from CX_4 to CH_4, and in passing from CH_2F_2 to CH_2I_2. In the absence of polarization data, these can perhaps be regarded only as tentative.[4]

5) CCl_2F_2, 6) CCl_2Br_2

The Raman spectrum of CCl_2F_2 has been studied by Bradley[1], and that of CCl_2Br_2 by Lecomte and his coworkers[2] who also examined the infrared spectrum of the molecule. In the absence of polarization data, we can only give the following tentative assignments in (145) and (146). Again we shall refer to the diagram (141) as a guide.



(145)



(146)

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[4] The assignments given here again differ somewhat from those of Barchewitz and Parodi, *loc. cit.* See footnote (4) in the preceding section on CH_2Cl_2.

[1] C. A. Bradley, Phys. Rev. 40, 908, (1932).

[2] J. Lecomte, H. Volkringer & A. Tchakrian, C. R. 204, 1929, (1937); Jour. de Phys. et Rad. 9, 105, (1938).

In CCl_2F_2, a line is found at 924 cm^{-1}, of intensity (2). Its frequency is too high for the missing fundamental in (145), but can be the combination frequency 664+260.

7) SO_2Cl_2

The Raman spectrum of this molecule was studied by Cabannes and Rousset[1]. From the degrees of depolarization, the following assignments can be made.

Vibration	cm^{-1}	I	ϱ
$\nu_1(s)$	1190	(1)	0.20
$\nu_2(s)$	560	(5)	0.06
$\delta_1(s)$	408	(10)	0.07
$\delta_2(s)$	214	(5)	0.70
$\nu_1(a)$	1415	(0)	6/7
$\nu_2(a)$	576	(0)	6/7
$\left\{\delta_1(a)\right.$	$\left\{390\right.$	(5)	6/7
$\delta_2(a)$	280	(2)	6/7
δ	365	(1)	6/7

Table LVII. Vibrational spectrum of SO_2Cl_2

E) $TZYX_2$ (symmetry C_{2v}) molecules

The only molecule belonging to this group is the ketene $OCCH_2$ molecule. The symmetry properties and the selection rules of the normal vibrations of this molecule are shown in Table LVIII.

Vibrations	class	Z-X	Z-Y	Z-axis	Infrared	Raman
ν_1 ν_2 ν_3 ν_4	A_1	*s*	*s*	*s*	$\mathfrak{M}_Z$	p
ν_5 ν_6 ν_7	B_1	*s*	*a*	*a*	$\mathfrak{M}_X$	d
ν_8 ν_9	B_2	*a*	*s*	*a*	$\mathfrak{M}_Y$	d

Table LVIII. Normal vibrations of $T-Z-YX_2$ molecule

The nature of the vibrations can be roughly described as follows: Of the 4 totally symmetrical vibrations, one is the symmetrical valence vibration ν_1 in CH_2, one the deformation vibration ν_2 in CH_2, one a valence vibration in C=C, and one a valence vibration in C=O. These will give the "*A*" type bands of an asymmetrical rotator. Of the 3 planar antisymmetrical vibrations in the class B_1, one is the antisymmetrical valence vibration ν_3 in CH_2, and the other two are roughly the perpendicular vibrations of the 4-particle system $(H_2)-C-C-O$. The two vibrations in the class B_2 are also perpendicular vibrations of $(H)_2-C-C-O$, but in directions perpendicular to the plane of the molecule. The bands in the classes B_1 and B_2 will be of the "*B*" and "*C*" types respectively. But by analogy with the formaldehyde OCH_2 molecule, one would expect the anisotropy of the motion perpendicular to the symmetry axis to be small, and the frequencies of the two B_2 vibrations would not be very different from those of the last two B_1 vibrations. The structure of the 5 vibrational bands in class B_1 and class B_2 will be that of the perpendicular bands of a linear molecule, since $I_A \ll I_B \sim I_C$.

---

[1] J. Cabannes & A. Rousset, Ann. de Physique 19, 229, (1933).

The infrared spectrum of ketene has been studied by Gershinowitz and Wilson[1] and the Raman spectrum by Kopper.[2] 11 absorption bands and 13 Raman lines are found; but as the infrared work has been reported only in a preliminary note and apparently done with instruments of low dispersion that did not permit a distinction between the parallel and the perpendicular type bands, and as no polarization measurements have been reported, it is not possible to give a definite assignment to the 9 fundamentals. The observed data and their tentative interpretations are summarized in Table LIX.

Assignment	Infrared freq.	Raman freq.
B_2 ν_9		510 (1b)
B_1 ν_7		599 (½b)
		715 (½b)
		801 (½b)
B_2 ν_8	890 s	
B_1 ν_6		998 (1)
A_1 ν_3	1110 s	1130 (6b)
	1185 ?	1198 (1)
	1325 w	
A_1 ν_2	1350 w	1344 (2)
	1400 s	1386 (1)
	1935 s	1895 (½)
A_1 ν_4	2160 s	2049 (½b)
A_1 ν_1	2915 w	2952 (5)
B_1 ν_5	3058 s	3015 (4b)
	3165 w	

Table LIX. Vibrational spectrum of ketene.

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[1] H. Gershinowitz & E. B. Wilson, Jr., Jour. Chem. Phys. 5, 500, (1937).

[2] H. Kopper, Zeits. f. phys. Chem. B 34, 396, (1936).

A normal coordinate treatment of the 4 totally symmetrical vibrations has been made by Thompson and Linnett[3] with the following modified valence force potential

$$2V = 2k(\delta r)^2 + k_1(\delta r_1)^2 + k_2(\delta r_2)^2 + k_\Theta(r\delta\vartheta)^2 + 2k_\varphi(s\delta\varphi)^2 + 2k_3(r\delta\Theta)\delta r_1 + 2k_4\,\delta r_1\,\delta r_2$$

where r, r_1, r_2 are the C−H, C−C, C−O distances respectively, Θ and φ are the H−C−H and H−C−C bond angles respectively. The determinantal equation is somewhat lengthy, and the four frequencies do not suffice for the determination of the 7 potential constants (of which k_Θ and k_φ enter as the combination $2k_\Theta + k_\varphi\,(s/r)^2$). On the assignments of these four frequencies as given in Table LIX and on certain assumptions as to the invariance of certain potential constants in passing from C_2H_4, OCH_2 to ketene, Thompson and Linnett obtained the following values for the constants,

$$k_{CH} = 4.85, \quad k_{CC} = 9.8, \quad k_{CO} = 12.3, \quad k_3 = 0.4,$$

$$2k_\Theta + k_\varphi\,(s/r)^2 = 0.96, \quad k_4 = 0.5 \times 10^5.$$

However, until the two low frequency B_1 fundamentals are definitely assigned, we shall regard these values of the potential constants as tentative only.

F) Molecules possessing no or low symmetries

1) $CHCl_2F$, 2) $CHCl_2Br$, 3) $CHBr_2Cl$, 4) $CHBr_2F$

The Raman spectrum of $CHCl_2F$ was studied by Bradley,[1] that of $CHBr_2F$ by Glockler and Backmann,[2] and those of $CHCl_2Br$ and $CHBr_2Cl$ by Emschwiller and Lecomte.[3] The assignment of the observed frequencies can be made on the following considerations: In these molecules, all the nine vibrations are distinct. They result from a splitting of the doubly degenerate vibrations in $CHCl_3$ and $CHBr_3$ when one of the 3 Cl or Br atoms is replaced by a different halogen atom. For comparison, the frequencies of $CHCl_3$ and $CHBr_3$ are also given in Table LX.

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[3] H. W. Thompson & J. W. Linnett, Jour. Chem. Soc. Lond. P. 1384, (1937).

[1] Bradley, C. A. Phys. Rev. 40, 908, (1932), assigned the 1215 and 366 cm^{-1} lines of $CHCl_3$ to a perpendicular and a parallel fundamental respectively. This and his correlation of the frequencies of $CHCl_3$ and $CHCl_2F$ need some modification, as shown in Table LX, in view of the polarization data in Table LIII.

[2] G. Glockler & J. H. Backmann, Phys. Rev. 54, 970, (1938).

[3] G. Emschwiller & J. Lecomte, Jour. de Phys. et Rad. 8, 130, (1937).

$CHCl_3$	$CHCl_2F$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_2F$	$CHBr_3$
668 ∥	723 (9)	610	568 *	619 (10)	539 ∥
761 ⊥	780 (4)	760	655 *	701 (1)	655 ⊥
	?	716		559 (3)	
366 ∥	454 (7)	329	(275)	358 (9)	222 ∥
262 ⊥	274 (7)	218		171 (9)	154 ⊥
	366 (4)	?	(201)	295 (5)	
3019 ∥	3019 (5)	3017		3017 (2)	3021 ∥
1215 ⊥	1065 (1)	1165	?	?	1144 ⊥
	1307 (3)	1204	1169 *	?	

Table LX. Raman spectra of $CHCl_2F$, $CHCl_2Br$, $CHBr_2$ Cl, $CHBr_2F$ Frequencies marked with * have been observed in absorption only.

The slight increase in the frequencies of $CHCl_2F$ relative to those of $CHCl_3$ is due to both the greater force constant for the C–F than for the C–Cl bond and the smaller mass of the F atom. Similarly for $CHBr_2F$ frequencies relative to those of $CHBr_3$. That the two frequencies of $CHBr_2F$ corresponding to the 1144 cm^{-1} of $CHBr_3$ have not been observed may be simply a question of intensity. Two lines at 93 and 3059 cm^{-1} observed in $CHBr_2F$ remain unaccounted for, since there is no place for either such a low or such a high frequency fundamental. In the case of $CHBr_2Cl$, only the infrared spectrum has been observed. The two frequencies 201 and 275 in parentheses are estimated from other weak absorption bands regarded as combinations of the fundamentals. Emschwiller and Lecomte assigned a weaker band at 737 cm^{-1} to one of the two frequencies corresponding to the 655 cm^{-1} of $CHBr_3$. It is seen however that this is a little too high on comparison with the corresponding frequencies in $CHBr_2F$. An examination of the Raman spectrum will be desirable to complete the systematics of the spectra of the trihalogen methanes.

5) HCOOH, 5a) HCOOD

The Raman spectrum of formic acid HCOOH has been studied by a number of workers,[1] and the infrared spectra of HCOOH and HCOOD have recently been studied by Bonner and by Hofstadter at room and at higher temperatures.[2] It was found that in passing from the low to high temperatures, the intense bands at *ca.* 3080 cm^{-1} in HCOOH and *ca.* 2347 cm^{-1} in HCOOD disappeared and gave rise to two bands at 3570 and 2940 cm^{-1} in HCOOH and at 2667 and 2950 cm^{-1} in HCOOD respectively. The explanation is that the bands at 3080 cm^{-1} in HCOOH and 2347 cm^{-1} in HCOOD have their origin in the hydrogen and deuterium bonds in the respective dimers[3]

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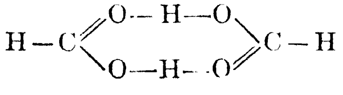
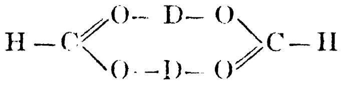
[1] Cf. Kohlrausch, *Der Smekal-Raman Effekt*, P. 315; also P. Koteswaram, Zeits. f. Physik 112, 395, (1939).





while the 3570 and 2667 cm^{-1} bands are due to the O−H and O−D bonds respectively in the single molecules, and the bands at *ca.* 2950 cm^{-1} are due to the C−H bonds (the C−H band 2940 cm^{-1} in HCOOH is masked by the H−bond band at 3080 cm^{-1} in the dimer).

In Table LXI, are summarized the infrared and Raman spectrum data and their interpretations. The Raman frequencies are for the dimers. As the infrared work was done with low dispersion and as it did not extend beyond 15μ, it is not possible to identify all the fundamental frequencies of the molecules.

Vibration	HCOOH	HCOOD	$(HCOOH)_2$		$(HCOOD)_2$
	Inf.	Inf.	Inf.	Ra.	Inf.
O−H	3570 *w*	2667 *m*			
C−H	2940 *m*	2950 *m*		2951	3000 *m*
O−H−O			3080 *s*		
O−D−O					2347 *s*
	2325				
					2105 *w*
C=O	1740 *s*	1764 *s*	1740 *s*	1647	1736 *s*
			1350 *s*	1392	1381 *m*
			1205 *s*	1196	1253 *s*
C−O	1093 *s*	1163 *s*	1093 *s*	1056	1181 *s*
		1030 *s*			1030 *s*
		980 *s*			
			917 *s*		
				793	
δ(OCO)	662 *s*	667 *w*	667 *s*	675	685 *w*
				511	

Table LXI. Vibrational spectra of HCOOH and HCOOD

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[2] L. G. Bonner & R. Hofstadter, Jour. Chem. Phys. 6, 531, (1938); Hofstadter, *ibid.*, 6, 540, (1938).

[3] See Chap. III, §5, B; L. Pauling and L. O. Brockway, Proc. Nat. Acad. Sci. 20, 336, (1934).

§4. Six-atomic Molecules

A) Linear Molecule

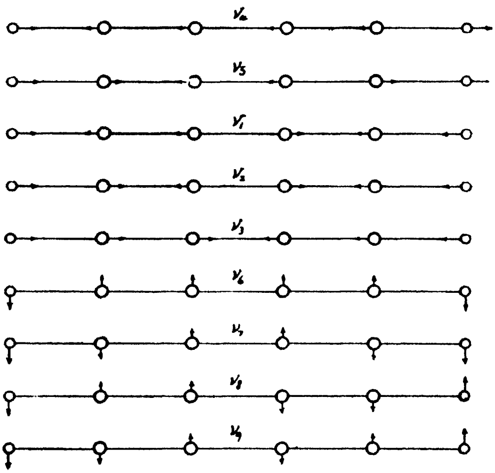

Fig. 34. Normal vibrations of diacetylene molecule

The only linear six-atomic molecule seems to be the diacetylene C_4H_2 molecule. That the Raman frequencies of this molecule have no corresponding infrared bands and vice versa shows that the molecule possesses a center of symmetry. A linear symmetrical *m-M-M-M-M-m* model has 5 parallel vibrations of which 3 are totally symmetrical and 2 antisymmetrical with respect to the center, and 4 doubly degenerate perpendicular vibrations of which 2 are symmetrical and 2 antisymmetrical with respect to the center. The general forms of the vibrations are shown in Fig. 34.

The selection rules for the fundamentals are as follows:

	ν_1, ν_2, ν_3	ν_4, ν_5	ν_6, ν_7	ν_8, ν_9
Infrared	inactive	parallel	perpendicular	inactive
Raman	p	inactive	inactive	d

The selection rules for the harmonic and combination bands are similar to those for C_2H_2 given in (82) of Chap. III.

The normal vibrations of this molecule has been treated by Wu and Shen.[1] For the parallel vibrations, they employed the potential

$$2V = k_1 x_3^2 + k_2 (x_2^2 + x_4^2) + k_3 (x_1^2 + x_5^2) + 2k_4 (x_1 x_2 + x_4 x_5)$$

$$+ 2k_5 (x_2 x_3 + x_3 x_4), \qquad (148)$$

---

[1] T. Y. Wu & S. T. Shen, Chin. Jour. Phys. 2, 128, (1936). A few numerical errors and misprints are corrected here.

where x_1, x_2, x_3, x_4, x_5 are the changes in the $m-M$, $M-M$, $M-M$, $M-M$, $M-m$ bond distances respectively. The determinantal equation gives for the 3 symmetrical vibrations

$$\lambda_1+\lambda_2+\lambda_3=\frac{2}{M}\left[k_1+k_2+\frac{M+m}{2m}k_3-k_4-2k_5\right],$$

$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1=\frac{2}{M^2}\left[(k_1k_2-2k_5^2)+\frac{M+m}{m}(k_1-2k_5)\,k_3\right.$$

$$\left.+\frac{2M+m}{2m}(k_2k_3-k_4^2)-2k_4(k_1-k_5)\right],$$

$$\lambda_1\lambda_2\lambda_3=\frac{2}{mM^2}\left[k_3(k_1k_2-2k_5^2)-k_1k_4^2\right], \tag{149a}$$

and for the 2 antisymmetrical vibrations

$$\lambda_4+\lambda_5=\frac{2}{M}\left[k_2+\frac{M+m}{2m}k_3-k_4\right],$$

$$\lambda_4\lambda_5=\frac{2M+m}{mM^2}(k_2k_3-k_4^2). \tag{149b}$$

For the perpendicular vibrations, the potential employed is

$$2V=k_{\alpha1}(\alpha_1^2+\alpha_2^2)+k_{\alpha2}(\alpha_2^2+\alpha_3^2)+2k_{\alpha3}(\alpha_1\alpha_2+\alpha_3\alpha_4)+2k_{\alpha4}\,\alpha_2\alpha_3 \tag{150}$$

where the α's are the changes in the angles between two successive bonds. The determinantal equation gives for the 2 symmetrical vibrations

$$\lambda_8+\lambda_9=\frac{1}{M(m+m\gamma^2+M\beta^2)}\left[\frac{m+M+(\beta+\gamma)^2M}{a^2}k_{\alpha1}\right.$$

$$+2\frac{\alpha m-\beta M+\beta(\alpha-\gamma)(\beta+\gamma)M}{ab}(k_{\alpha1}-k_{\alpha3})-\frac{4(\gamma m-\beta M)}{ac}k_{\alpha3}$$

$$+\frac{\alpha^2 m+\beta^2[1+(\alpha-\gamma)^2]M}{b^2}(k_{\alpha 1}+k_{\alpha 2}-2k_{\alpha 3}-k_{\alpha 4})$$

$$+\frac{4(\alpha\gamma m+\beta^2 M)}{bc}(k_{\alpha 2}-k_{\alpha 3}-k_{\alpha 4})+\frac{4(\gamma^2 m+\beta^2 M)}{c^2}(k_{\alpha 2}-k_{\alpha 4})\Bigg], \tag{151a}$$

$$\lambda_8\cdot\lambda_9=\frac{1}{M(m+m\gamma^2+M\beta^2)}\left[\frac{1}{a^2}\left\{\frac{\alpha+\beta}{b}+\frac{2(\beta+\gamma)}{c}\right\}^2+\frac{4\beta(\alpha-\gamma)}{abc}\right.$$

$$\left.\left\{\frac{\alpha+\beta}{b}+\frac{2(\beta+\gamma)}{c}\right\}+\frac{4(\alpha\beta-\beta\gamma)^2}{a^2c^2}\right](k_{\alpha 1}k_{\alpha 2}-k_{\alpha 1}k_{\alpha 4}-k_{\alpha 3}^2),$$

where $\alpha=2\left(1+\frac{b}{c}\right)$, $\beta=\frac{m}{M}\left(\frac{2a+2b+c}{c}\right)$, $\gamma=\frac{2b+c}{c}$ and a, b, c are the normal bond distances H$-$C, C$\equiv$C, C$-$C respectively. For the 2 antisymmetrical vibrations,

$$\lambda_6+\lambda_7=\frac{M+m}{mM}\ \frac{k_{\alpha 1}}{a^2}+\frac{2}{M}\ \frac{k_{\alpha 1}+k_{\alpha 2}-2k_{\alpha 3}+k_{\alpha 4}}{b^2}+\frac{2}{M}\ \frac{k_{\sigma 1}-k_{\alpha 3}}{ab},$$

$$\lambda_6\cdot\lambda_7=\frac{2M+m}{mM^2}\ \frac{k_{\alpha 1}k_{\alpha 2}+k_{\alpha 1}k_{\alpha 4}-k_{\alpha 3}^2}{(ab)^2}. \tag{151b}$$

From the nine frequencies, the nine constants in the potentials (148) and (150).

The infrared spectrum of C_4H_2 was studied by Bartholomé and Karweil,[2] and the Raman spectrum by Timm and Mecke.[3] The observed frequencies and their assignments are summarized in Table LXII.

[2] E. Bartholomé, Zeits. f. phys. Chem. B 23, 152, (1932); Bartholomé and J. Karweil, *ibid.*, B 35, 442, (1937).

[3] B. Timm & R, Mecke, Zeits. f. Physik 94, 1, (1935).

Obs.	ν	Timm & Mecke	Wu & Shen	Bartholomé & Karweil
(3350)		ν_1	ν_1	ν_1
2183	Ra.	ν_2	ν_2	ν_2
644	Ra.	ν_3	ν_3	ν_3
3350	Inf.	ν_4	ν_4	ν_4
2024	Inf.	ν_5	ν_5	ν_5
		$(\nu_8 \sim 720)$	$(\nu_7 \sim 460)$	$(\nu_9 \sim 720)$
230w	Ra.	ν_7	ν_9	$\nu_9 - \nu_8$
411w	Ra.	$\nu_3 - \nu_7$	$\nu_3 - \nu_9$	$\nu_3 + \nu_8 - \nu_9$
488	Ra.	ν_9	ν_8	ν_8
690	Inf.		$\nu_7 + \nu_9$	ν_6
708	Inf.	$\nu_6 \sim 730$	ν_6	ν_7
1235	Inf.	$\nu_6 + \nu_9$	$\nu_6 + \nu_8$	$\nu_6 + \nu_8, \nu_7 + \nu_8$
1440	Inf.	$\nu_6 + \nu_8$	$\nu_7 + 2\nu_8$	$\nu_6 + \nu_9, \nu_7 + \nu_9$
2950w	Inf.			$\nu_2 + \nu_6$
2980w	Inf.			$\nu_2 + \nu_7$
3030w	Inf.			$\nu_2 + 2\nu_8$
3120w	Inf.		$\nu_4 - \nu_9$	$\nu_3 + \nu_5 + \nu_8$
3550w	Inf.		$\nu_4 + \nu_9$	$\nu_5 + 2\nu_9$
3920w	Inf.		$\nu_3 + \nu_4$	$\nu_3 + \nu_9$
6500w	Inf.	$\nu_1 + \nu_4$	$\nu_1 + \nu_4$	$\nu_1 + \nu_4$
8950?	Inf.		$\nu_1 + \nu_2 + \nu_4$	$\nu_1 + \nu_2 + \nu_4$

Table LXII. Vibrational spectrum of C_4H_2

Consider first the parallel fundamentals. The symmetrical frequency ν_1 has not been observed in the Raman spectrum, but is expected to lie in the neighborhood of 3350 cm^{-1}. The Raman frequency 644 cm^{-1} appears a little too low for the symmetrical C–C vibration; but the observation of Woo and Chu[4] on the ultraviolet bands of C_4H_2 at different temperatures shows that 644 cm^{-1} is a fundamental frequency in the normal electronic state of the molecule. With the 5 parallel fundamentals in Table LXII, the constants in (148) can be determined by means of (149). They are

$$k_{C\text{-}C} = 3.58, \qquad k_{C\equiv C} = 16.3, \qquad k_{CH} = 5.95,$$
$$k_4 = 0.71, \qquad k_5 = 0.71. \tag{152}$$

The C–C bond constant is considerably lower than the value $\sim 5 \times 10^5$ usually associated with single bond C–C and may indicate a different electronic structure in the bond. Recently, from electron diffraction measurements Pauling and his coworkers[5] found the following values for the bond distances in C_4H_2

---

[4] S. C. Woo & T. C. Chu, Jour. Chem. Phys. 5, 786, (1937).

[5] L. Pauling, H. D. Springall & K. J. Palmer, Jour. Am. Chem. Soc. 61, 927, (1939).

$$r\,(\mathrm{C-C}) = 1.36 \pm .03\ \text{Å}, \qquad r\,(\mathrm{C \equiv C}) = 1.187\ \text{Å}, \tag{153}$$

The C–C bond distance indicates, according to Pauling's relation between bond lengths and bond structure, some contributions from double bond C=C arising from resonance. But then the low value for the bond constant above seems difficult to understand.

For the perpendicular fundamentals, the assignments are more difficult. Timm and Mecke based their assignments on the similarity between C_4H_2 and C_2N_2, the two molecules being isoelectronic. The objections are (*i*) that the assignment of the Raman line 230 cm^{-1} to the antisymmetrical vibration ν_7 is at variance with the selection rules, and (*ii*) that the assumed $\nu_8 \sim 720$ was not observed in the Raman spectrum. The assignments of Bartholomé and Karweil are also based on a comparison with the C_2N_2 molecule, with Eucken-Bertram's assignment for the deformation vibrations (see Table XXVI). The objections are that (*i*) the value $\nu_4 \sim 740$ for C_2N_2 is probably incorrect, and (*ii*) their assignments lead to no real values for the potential constants in (150). The assignments suggested by Wu and Shen were aimed at removing the difficulty with the selection rules, the value $\nu_7 \sim 460\ \mathrm{cm}^{-1}$ being based on the identification of the infrared band at 690 cm^{-1} with $\nu_7 + \nu_8$. They yield, however, no real values for the constants in the potential (150). With Timm and Mecke's frequencies, equations (151) give

$$\begin{aligned} k_{\alpha 1} &= 2.8, & k_{\alpha 2} &= 3.2, \\ k_{\alpha 3} &= 0.54, & k_{\alpha 4} &= 0.24 \times 10^{-12}. \end{aligned} \tag{154}$$

While there is no check for these values, they seem to be of the correct order of magnitude, on consideration of the deformation constants in other molecules (C_2N_2, C_3O_2 and the linear triatomic molecules in §1). For this reason, their assignments are to be preferred, although further investigation, especially on the Raman spectrum and polarization measurements, seem still desirable.

B) Plane Symmetrical Y_2X_4 Molecules

A molecule of the ethylene C_2H_4 type belongs to the symmetry class V_h. It possesses 3 mutually perpendicular planes of symmetry.

The symmetry properties and the selection rules for the 12 normal vibrations are given in Table LXIII.[1]

Vibrations	Symmetry class	X-Y	Y-Z	Z-X	Infrared	Raman
$\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$	A_{1s}	s	s	s	ina.	p
$\nu_{\pi a}$, $\delta_{\pi a}$	A_{2a}	a	s	s	$\mathfrak{M}_z$	ina.
$\nu_{\sigma s}$, $\delta_{\sigma s}$	B_{2s}	a	a	s	ina.	d
$\nu_{\sigma a}$, $\delta_{\sigma a}$	B_{1a}	s	a	s	$\mathfrak{M}_x$	ina.
$\delta_{\sigma' s}$	B_{1s}	a	s	a	ina.	d
$\delta_{\sigma' a}$	B_{2a}	s	s	a	$\mathfrak{M}_y$	ina.
torsion(δ)	A_{1a}	a	a	a	ina.	ina.

Table LXIII. Normal vibrations of ethylene type molecules
For the coordinate planes X–Y, Y–Z, Z–X, see Fig. 7

The general forms of the normal vibrations are shown in Fig. 35. It is seen that the infrared active bands are of the *A*, *B*, *C* types of an asymmetrical rotator according as whether the change of the electric moment is along the axis of least, intermediate or greatest moment of inertia.

The selection rules for the harmonic and combination bands can be obtained on the following considerations: The symmetry property of a combination or harmonic level is the product of the symmetry properties of the fundamentals. From this, it immediately follows that no first harmonic of any fundamental is active in absorption.

The normal vibrations of the Y_2X_4 type molecule have been treated by a number of authors using different potential functions. For the 5 vibrations $\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$, $\nu_{\pi a}$, $\delta_{\pi a}$, Sutherland and Dennison introduced the following potential[2]

$$2V = a\,(x_1^2 + x_2^2) + b\,(y_1^2 + y_2^2) + cx^2 + 2d(x_1y_1 + x_2y_2) + 2e(x_1 + x_2)x, \quad (155)$$

---

[1] The notations for the normal vibrations are those of Mecke. They are preferred to the conventional numerical notations because they are more descriptive of the symmetry and the nature of the vibrations. It must be remembered, however, that the distinction between the "valence" and the "deformation" vibrations implied by the notations is never sharp, and is in fact not possible in such molecules as C_2Cl_4.

[2] Sutherland & Dennison, Proc. Roy. Soc. A 148, 250, (1935), with $e=0$.

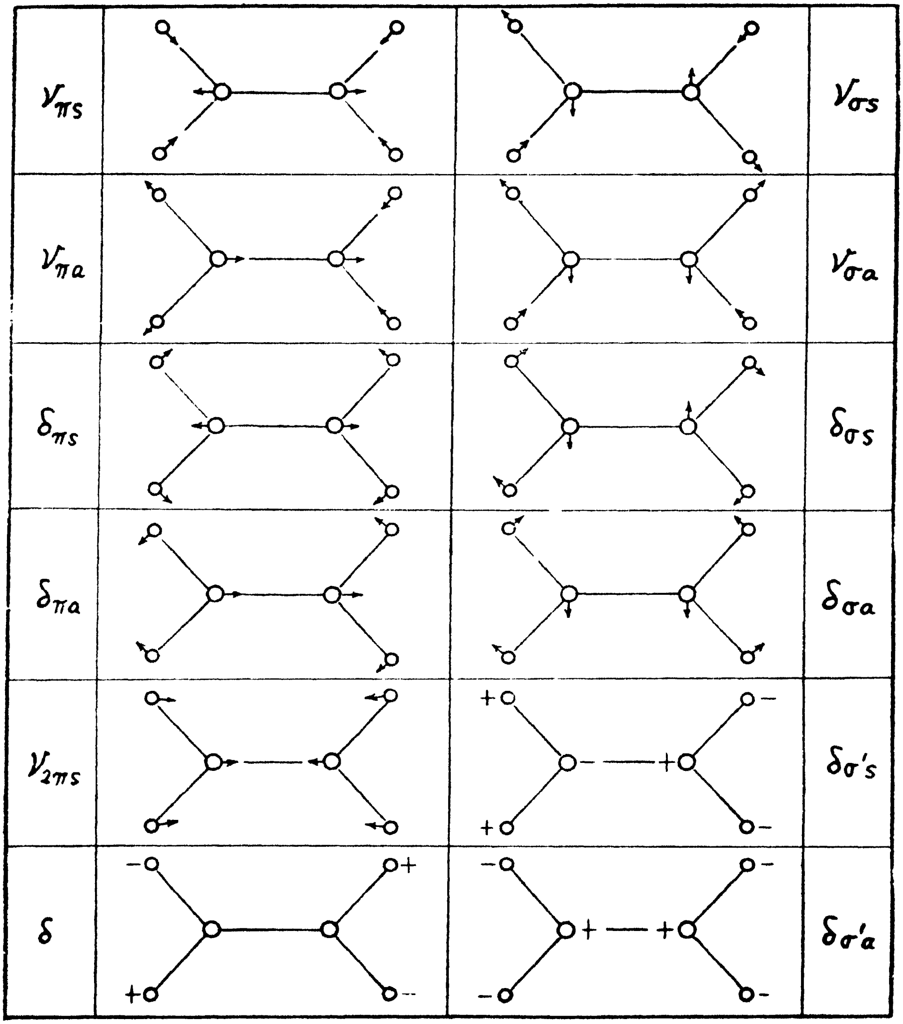

Fig. 35. Normal vibrations of ethylene type molecules. + and − indicate displacements in and out of the plane of paper.

where x_1, x_2 are the displacements of the Y atoms relative to the centers of gravity of their respective neighboring X atoms, x is the displacement between the 2 Y atoms, and y_1, y_2 are the displacements between the 2 X atoms in each YX_2 group. The determinantal equation gives for the symmetrical vibrations $\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$,

$$\begin{aligned}\lambda_1+\lambda_2+\lambda_3 &= \frac{M+2m}{2mM}\,a+\frac{2}{m}\,b+\frac{2}{M}(c-2e)\,,\\ \lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1 &= \frac{M+2m}{m^2M}\,(ab-d^2)+\frac{4}{mM}(c-2e)b+\frac{ac-2e^2}{mM}\,, \qquad (156)\\ \lambda_1\lambda_2\lambda_3 &= \frac{2}{m^2M}\Big[(ab-d^2)\,c-2be^2\Big].\end{aligned}$$

The equations for the antisymmetrical vibrations $\nu_{\pi a}$, $\delta_{\pi a}$ are obtained from (156) by setting $c=e=0$.

If the interaction between the Y atom of one YX_2 group and the X atoms of the other group is very small so that e may be set equal to zero, then one obtains the relation

$$\frac{M+2m}{M}\;\frac{\lambda_1\lambda_2\lambda_3}{\lambda_4\lambda_5}=\lambda_1+\lambda_2+\lambda_3-\lambda_4-\lambda_5, \qquad (157)$$

which may be used for estimating one of the fundamentals when the other four are known, or as a check for the assumption $e=0$ when all the 5 frequencies are known.

For all the normal vibrations except δ of the Y_2X_4 molecule, Wilson suggested the potential[3]

$$\begin{aligned}2V &= k\,\Sigma\,(\delta r_i)^2+k_1\,(\delta r)^2+Ha^2\,\Sigma\,(\delta\alpha_i)^2+2k_2\,(\delta r_1\delta r_2+\delta r_3\delta r_4)+ha^2\,\Sigma\,(\delta\beta_i)^2\\ &\quad+2\Theta a^2(\delta\alpha_1\delta\alpha_2+\delta\alpha_3\delta\alpha_4)+2\lambda a^2(\delta\alpha_1\delta\alpha_3+\delta\alpha_2\delta\alpha_4)+2\Omega a^2(\delta\beta_1\delta\beta_3+\delta\beta_2\delta\beta_4). \qquad (158)\end{aligned}$$

where α_1, α_2, α_3, α_4 are the angles which the Y−X bonds make with the Y−Y axis, $\delta\beta_1 \cdots\cdots \delta\beta_4$ the angles of bending of the Y−X bonds from the plane of the molecule, and the δr's have the usual meanings. With the notations

$$\begin{aligned}&N=\frac{1}{m}+\frac{2}{M}\sin^2\alpha\,, \qquad P=\frac{2}{M}\cos\alpha\sin\alpha\,, \qquad Q=\frac{1}{m}+\frac{2}{M}\cos^2\alpha\,,\\ &E=\frac{2}{M}\cdot\frac{a+b\cos\alpha}{b}\sin\alpha,\; F=\frac{1}{m}+\frac{2}{M}\left(\frac{a+b\cos\alpha}{b}\right)^2,\, G=\frac{M+2m}{mM}, \qquad (159)\end{aligned}$$

the determinantal equation gives for $\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$,

$$\begin{aligned}\lambda_1+\lambda_2+\lambda_3 &= \frac{2}{M}k_1+Q\,(k+k_2)+N\,(H+\Theta+\lambda)\\ \lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1 &= \frac{2}{mM}\Big[k_1(k+k_2)+\Big\{k_1+\tfrac{1}{2}MG(k+k_2)\Big\}(H+\Theta+\lambda)\Big] \qquad (160a)\\ \lambda_1\lambda_2\lambda_3 &= \frac{2}{m^2M}k_1\,(k+k_2)\,(H+\Theta+\lambda)\end{aligned}$$

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[3] **E. B. Wilson, quoted in L. G. Bonner, Jour. Am.** Chem. Soc. 58, 34, (1936).

for $\delta_{\pi a}$, $\delta_{\pi a}$,

$$\lambda_4 + \lambda_5 = Q\,(k + k_2) + N\,(H + \theta - \lambda)$$

$$\lambda_4\,\lambda_5 = \frac{1}{m}\,G\,(k + k_2)\,(H + \theta - \lambda), \tag{160b}$$

for $\nu_{\sigma s}$, $\delta_{\sigma s}$,

$$\lambda_6 + \lambda_7 = N\,(k - k_2) + F\,(H - \theta - \lambda)$$

$$\lambda_6 \cdot \lambda_7 = (NF - E^2)\,(k - k_2)\,(H - \theta - \lambda), \tag{160c}$$

for $\nu_{\sigma a}$, $\delta_{\sigma a}$,

$$\lambda_8 + \lambda_9 = N\,(k - k_2) + Q\,(H - \theta + \lambda)$$

$$\lambda_8\,\lambda_9 = \frac{1}{m}\,G\,(k - k_2)\,(H - \theta + \lambda), \tag{160d}$$

for $\delta_{\sigma' s}$,

$$\lambda_{10} = \frac{2md^2 + Mb^2}{mMb}\,(h - \Omega), \tag{160e}$$

for $\delta_{\sigma' a}$,

$$\lambda_{11} = G\,(h + \Omega), \tag{160f}$$

where 2b is the Y−Y distance, and $d = a \sin \alpha + b$.

Still another potential of the valence force type has been used by Thompson and Linnett, and by Fox and Martin.[4] It is

$$2V = k\,\Sigma\,(\delta r_i)^2 + k_1\,(\delta r)^2 + 2k_\theta\,a^2\,(\delta\theta)^2 + 4k_\varphi s^2\,\Sigma\,(\delta\varphi_i)^2$$
$$+ 2k_3 a\left[\,(\delta\theta_1) + (\delta\theta_2)\,\right]\delta r + 2k_2\,(\delta r_1\,\delta r_2 + \delta r_3\,\delta r_4), \tag{161}$$

where θ is the angle between the 2 Y−X bonds and $\theta + 2\varphi = 2\pi$. The determinantal equation gives for $\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$,

$$\lambda_1 + \lambda_2 + \lambda_3 = \frac{2}{M}\,k_1 + Q(k + k_2) + Nk_\alpha + Wk_3,$$

$$\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1 = \frac{2}{mM}\left[k_1\,(k + k_2) + \left\{k_1 + \tfrac{1}{2}MG\,(k + k_2)\right\}k_\alpha + \frac{M}{2}Wk_3\,(k + k_2) - k_3^2\right]$$

$$\lambda_1\lambda_2\lambda_3 = \frac{2}{m^2M}(k + k_2)(k_1k_\alpha - k_3^2)\,, \tag{162a}$$

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[4] H. W. Thompson & J. W. Linnett, Jour. Chem. Soc. Lond. P. 1376, (1937); The term in k_2 was added by J. J. Fox & A. E. Martin, Proc. Rev. Soc. A 167, 257, (1938).

for $\nu_{\pi a}$, $\delta_{\pi a}$,

$$\lambda_4 + \lambda_5 = Q\,(k + k_2) + N k_\alpha$$

$$\lambda_4 \lambda_5 = \frac{1}{m} G\,(k + k_2)\, k_\alpha \tag{162b}$$

where

$$k_\alpha = 2k_\Theta + k_\varphi\,(s/a)^2, \qquad W = \frac{8}{M} \sin\frac{\Theta}{2}$$

and Q, N have the same meaning as in (159). For $\nu_{\sigma s}$, $\delta_{\sigma s}$, the relations are

$$\lambda_6 + \lambda_7 = N\,(k - k_2) + F\, k_\varphi\,(s/a)^2$$

$$\lambda_6 \lambda_7 = (NF - E^2)\,(k - k_2)\, k_\varphi\,(s/a)^2\,, \tag{162c}$$

and for $\nu_{\sigma a}$, $\delta_{\sigma a}$,

$$\lambda_8 + \lambda_9 = N\,(k - k_2) + Q\, k_\varphi\,(s/a)^2\,,$$

$$\lambda_8 \lambda_9 = \frac{1}{m} G\,(k - k_2)\, k_\varphi\,(s/a)^2\,. \tag{162d}$$

Manneback and Verleysen have employed for the C_2H_4 molecule a potential containing 11 constants. With such a potential, they have calculated the 9 planar vibrations of deutero-ethylenes. We shall come to their results later.

It may perhaps be emphasized that since each of the potentials mentioned above is less general than what is demanded by general symmetry considerations, their success or failure must be judged by a comparison with the empirical data. It may well be that a different potential must be used in a different molecule. We shall see that this is in fact the case.

In molecules of the C_2H_4 type, there is a torsional vibration which is inactive in both the absorption and the Raman spectra. It contributes, however, to the molecular heat of the molecule. When all the other fundamental frequencies are known from the infrared and the Raman spectra, it is possible to determine the frequency of the torsional vibration from the specific heat data, especially at low temperatures.

1) C_2H_4

The infrared spectrum has been studied by Levin and Meyer,[1] and the photographic region by Bonner.[2] The Raman spectrum has been studied by a number of authors[3]–[7]. The observed data are summarized in Tables LXIII and LXIV.

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[1] A. A. Levin & C. F. Meyer, Jour. Am. Opt. Soc. 16, 137, (1928).

[2] L. G. Bonner, Jour. Am. Chem. Soc. 58, 34, (1936).

	gas C_2H_4 (3)	gas C_2H_4 (4)	liquid C_2H_4 (5)	liquid C_2H_4 (2)	liquid C_2H_4 (6)	liquid C_2H_4 (7)
$\delta_{\sigma s}$				950	944	943
$\delta_{\pi s}$	1342	1343	1340	1341	1341	1341
$\nu_{2\pi s}(C^{12}—C^{13})$						1602*w*
$\nu_{2\pi s}$	1623	1626	1620	1619	1620	1621
2δ		1656 *w*		1654*w*		1653*w*
$2\delta_{\pi a}$	2880 *w*	2880 *w*		2880*w*		2870*w*
$\nu_{\pi s}$ $(C^{12}—C^{13})$						2997*vw*
$\nu_{\pi s}$	3019	3020	3000	3009	3007	3008
$\nu_{\sigma a}$?			3080	3069 *w*	3072*w*	3075*w*
$2\nu_{2\pi s}$	3240 *vw*					3230*vw*
$\nu_{\sigma s}$	3272 *vw*					3263*vw*

Table LXIVa. Raman spectrum of C_2H_4

Obs.ν				Obs.ν		
950	*Z*		$\delta_{\sigma' a}$	8775	*Z*	$3\nu_{\pi a}$
1444	*Z*		$\delta_{\pi a}$	8981	*Z*	$\nu_{\pi a}+2\nu_{\sigma a}$
1889	*Z*	*m*	$\nu_{\pi a}-\delta_{\sigma' s}$	9138	*D*	$3\nu_{\sigma a}$
2047	*Z*	*w*	$\delta_{\sigma' a}+\delta_{\sigma' s}$	9775	*Z*	$2\nu_{\pi a}+\left\{\begin{matrix}\nu_{\sigma a}+\delta_{\sigma s}\\ \nu_{\sigma s}+\delta_{\sigma a}\end{matrix}\right.$
2325		*vw*		9814	*Z*	
2988	*Z*		$\nu_{\pi a}$	10119	*D*	$2\nu_{\pi a}+\nu_{\sigma a}+\delta_{\pi s}$
3107	*D*		$\nu_{\sigma a}$	10293	*Z*	$\nu_{\pi a}+2\nu_{\sigma a}+\delta_{\pi s}$
4207	*D*	*w*	$\delta_{\pi s}+3\,\delta_{\sigma a}$	10363	*Z*	$3\nu_{\pi a}+\nu_{2\pi s}$
4324	*D*	*m*	$\delta_{\sigma a}+3\,\delta_{\sigma s}$	11465	*D*	$2\nu_{\pi a}+\nu_{\sigma a}+2\delta_{\pi s}$
4515	*D*	*m*		11724	*Z*	$3\nu_{\pi a}+\nu_{\pi s}$
4729	*D*	*w*	$\delta_{\pi a}+\nu_{\sigma s},\nu_{\sigma a}+\nu_{2\pi s}$	11780	*D*	$3\nu_{\pi a}+\nu_{\sigma s}$
4930				14100	?	$5\nu_{\pi a}$
5050						
5061						

Table LXIVb. Absorption spectrum of C_2H_4

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[3] Dickenson, Dillon & Rasetti, Phys. Rev. 34, 582, (1929).

[4] S. Bhagavantam, Nature 138, 1096, (1936).

[5] P. Daure, Ann. de Physique 12, 375, (1929).

[6] de Hemptinne, Jungers & Delfosse, Jour. Chem. Phys. 6, 319, (1938).

[7] G. Glockler & M. Renfrew, Jour. Chem. Phys. 6, 170, 409, (1938).

Consider first the assignments of the fundamental frequencies. There is no doubt that the 3 strong Raman lines at 3019, 1342, 1623 cm^{-1} are due to the 3 totally symmetrical vibrations $\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$, and that the 2 intense infrared bands at 2988 and 1444 cm^{-1} possessing sharp Q branches are due to $\nu_{\pi a}$ and $\delta_{\pi a}$, since these bands are of the A type of an asymmetrical rotator. The band at 3107 cm^{-1} with a doublet structure is without doubt $\nu_{\sigma a}$ which should be of the B type. The intense band at 950 cm^{-1} with a Q branch can be ascribed to $\delta_{\sigma' a}$ which is of the C type. From the nature of the vibration $\delta_{\sigma a}$, it seems very unlikely that it is very much different in frequency from $\delta_{\sigma' a}$. As no other band is observed in the region from 700 to 1400 cm^{-1}, it is probable that $\delta_{\sigma a}$ is overlapped by $\delta_{\sigma' a}$ at 950 cm^{-1}. The assignments of the 3 frequencies $\nu_{\sigma s}$, $\delta_{\sigma s}$, $\delta_{\sigma' s}$ are less definite. The Raman frequency 3070 cm^{-1} of the liquid has been assigned by Bonner and by de Hamptinne and his coworkers to $\nu_{\sigma s}$. There is the difficulty, however, that it is not observed in the gas although the weak lines 3270 and 3240 cm^{-1} do appear in the gas. Glockler and Renfrew suggested that the 3070 line may be due to the infrared active fundamental which is rendered Raman effect active by perturbations existing in the liquid state. On accepting this, one may assign the Raman frequency 3272 cm^{-1} of the gas to $\nu_{\sigma s}$ and 3240 to $2\nu_{2\pi s}$. The frequency $\delta_{\sigma s}$ is expected to be of the same order as $\delta_{\sigma a}$, and the Raman line 944 of the liquid can be assigned to it although there is again the difficulty that it is not found in the gas. The frequency $\delta_{\sigma' s}$ can be estimated by means of the relations (160e) and (160f) with approximate values for the molecular dimensions and the assumption that the constant Ω is small compared with the constant h in (158). Thus one finds $\delta_{\sigma' s} \sim 1100$ cm^{-1}. With this value, it is easy to explain the weak infrared band at 2047 cm^{-1} as $\delta_{\sigma' a} + \delta_{\sigma' s}$.

For the torsional vibration δ, Eucken and Parts have estimated the frequency at 745-800 cm^{-1} from their measurements on the specific heats of C_2H_4 down to 190° K[8]. On this basis, it is possible to explain the weak Raman line at 1656 cm^{-1} as the first harmonic of δ which is active on symmetry considerations. In fact it would be difficult to explain this Raman line in any other manner.

With the above fundamentals, a reasonable assignment can be given to all the observed frequencies in the Raman and the absorption spectra, as shown in Tables LXIV*a* and LXIV*b*, although the assignments of the high combination bands are not unique on account of the closeness of some of the fundamentals.

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[8] A. Eucken & A. Parts, Zeits. f. phys. Chem. B 20, 184, (1933).

The constants in the potential (155) can be calculated. They are

$$a = 7.53, \quad b = 1.05, \quad c = 9.74, \quad d = \pm 1.53, \quad e = 0.705. \tag{163}$$

The constants in the potential (161) together with the angle Θ between the two C–H bonds can be calculated from (162a), (162b) and (162c). They are

$$\begin{aligned} &k_{CH} = 5.28, \quad k_{CC} = 9.77, \quad k_8 = -0.51 \quad k_2 = -0.34, \\ &k_\Theta = 0.405, \quad k_\varphi (s/a)^2 = 0.306, \quad \Theta = 107°. \end{aligned} \tag{164}$$

Similar calculations with equations (160) do not yield consistent values for the constants in the potential (158). As the values of the potential constants are rather sensitive to the frequencies and as some of the fundamentals are not known accurately, especially on account of the anharmonicity, it does not seem worth while to stress too much on the exact values of the potential constants.

The potential of Manneback and Verleysen[9] containing 11 constants for the 9 planar vibrations no doubt gives a better description of the molecule. As we shall see below, even such a potential is not completely satisfactory since the calculated frequencies of the deutero-ethylenes differ by as much as 50 cm^{-1} in some cases.

Concerning the dimensions of the C_2H_4 molecule, the following may be said: From the photographic bands of the molecule, Badger[10] gave the following moments of inertia of the molecule[11]

$$I_A = 5.70, \quad I_B = 27.5, \quad I_C = 33.2 \times 10^{-40}\,\text{g.cm.}^2 \tag{165}$$

These values are not sufficient to determine uniquely the C–H, C–C distances and the H–C–H bond angle. Penney[12] argued that the C–H distance in C_2H_4 must lie between the value 1.06 Å in C_2H_2 (64) and the value 1.09 Å in CH_4 (128b) and assumed the value 1.08 Å. Then (165) leads to the following values

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[9] C. Manneback & A. Verleysen, Ann. Soc. Sci. Bruxelles B 56, 349, (1936); Verleysen & Manneback, *ibid.*, 57, 31, (1937); Nature 138, 367, (1936).

[10] R. M. Badger, Phys. Rev. 45, 648, (1934), gave the following values: $r(C-H) = 1.04$ Å, $r(C=C) = 1.37$ Å and $\Theta = 126°$. The C–H distance is too small.

[11] W. Scheibe & P. Lueg, Zeits. f. Physik 81, 764, (1933), analyzed the 11465 cm^{-1} band of C_2H_4 and obtained the value 28.25×10^{-40} g.cm^2 for the moment of inertia of the molecule. But the analysis is based on treating the molecule as linear and hence the result is incorrect.

[12] W. G. Penney, Proc. Roy. Soc. A 158, 306, (1937).

$$r\,(C-H) = 1.08\,\text{Å}, \qquad r\,(C=C) = 1.33\,\text{Å}, \qquad \theta = 118^\circ \qquad (166)$$

la, b, c, d, e, f) C_2H_3D, *cis, trans* & asym, $C_2H_2D_2$, C_2HD_3, C_2D_4

While the molecules C_2H_3D and C_2HD_3 have no symmetry and hence all the normal vibrations are active in both the absorption and the Raman spectra, the cis $C_2H_2D_2$ and the asymmetrical $C_2H_2D_2$ belong to the symmetry class C_{2v} and the trans $C_2H_2D_2$ to C_{2h}. The selection rules for these molecules are given in Table LXV. For convenience, the vibrations are given the same notations as for the corresponding vibrations in C_2H_4.

Vibrations	trans Inf.	 Ra.	cis Inf.	 Ra.	asym. Inf.	 Ra.
$\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$	ina.	p	*B*	p	*A*	p
$\nu_{\pi a}$, $\delta_{\pi a}$	act.	ina.	*A*	d	*A*	p
$\nu_{\sigma s}$, $\delta_{\sigma s}$	ina.	p	*A*	d	*B*	d
$\nu_{\sigma a}$, $\delta_{\sigma a}$	act.	ina.	*B*	p	*B*	d
$\delta_{\sigma' s}$	ina.	d	ina.	d	*C*	d
$\delta_{\sigma' a}$	act.	ina.	*C*	d	*C*	d
torsion δ	act.	ina.	ina.	d	ina.	d

Table LXV. Selection rules of deutero-ethylenes.
A, B, C means that the band is of the *A, B,* or *C* type of an asymmetrical rotator.

The Raman spectra of the deutero-ethylenes have been studied by de Hemptinne, Jungers and Delfosse[1], and the infrared spectrum of C_2D_4 has been studied by Sutherland and Conn[2]. In Table LXVI are summarized the observed frequencies together with the calculated values obtained by Manneback, Verleysen and their coworkers.[3]

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[1] M. de Hemptinne, C. Jungers & J. M. Delfosse, Jour. Chem. Phys. 6, 319, (1938).

[2] G. B. B. M. Sutherland & G. K. T. Conn, Nature, 140, 644, (1937); Conn & Sutherland, Proc. Roy. Soc. A abstract 17, March, (1939).

[3] See footnote (9) of last section.

	C_2H_4	C_2H_3D	trans $C_2H_2D_2$	cis $C_2H_2D_2$	asym $C_2H_2D_2$	C_2HD_3	C_2D_4
$\nu_{\pi s}$	3020	2964.7 (2986)	2275.9 (2291)	2290.1 (2304)	(3001)		2251.8 (2284)
$\nu_{2\pi s}$	1623	1600.2 (1570)	1567.3 (1514)	1567.3 (1516)	1581.4 (1555)	1514.4	1514.5 (1429)
$\delta_{\pi s}$	1343	1286.2 (1262)	1215.0 (1240)	1282.2 (1247)	(1013)	995.2	981.3 (1009)
$\nu_{\pi a}$	2988	2266.4 (2255)	(2233)	(2229)	2221.0 (2221)	2215.0	2192.3 Inf. (2153)
$\delta_{\pi a}$	1444	1396.6 (1380)	(1308)	(1295)	1379.1 (1358)		1077.4 Inf. (1073)
$\nu_{\sigma s}$	3272?		3033.1 (3049)	(3031)	(3088)		2306 (2308)
$\delta_{\sigma s}$	950		863.4 (808)	(820)	(946)		780 (758)
$\nu_{\sigma a}$	3107	3015.3 (3031)	(3053)	3046.4 (3065)	(2316)	2272.6	2335.5 Inf. (2325)
$\delta_{\sigma a}$	950		(765)	763.4 (753)	(725)		(678)
$\delta_{\sigma' s}$	1100						
$\delta_{\sigma' a}$	950						719.5 Inf. (719)
δ	828						

Table LXVI. Vibrational spectra of deutero-ethylenes. Calculated frequencies are given in parentheses.

The assignments of the frequencies are guided by (*i*) considerations of the symmetry properties and the selection rules for the various molecules, and (*ii*) regarding the cis and trans $C_2H_2D_2$ as made up of two CHD radicals and estimating the frequencies of the CHD group[4]. For C_2H_3D and C_2HD_3, the assignments are based on considering the trend of the frequencies of the various vibrations in passing from C_2H_4 to C_2D_4.

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[4] T. Y. Wu, Jour. Chem. Phys. 5, 392, (1937).

In C_2D_4, the calculated frequency 719 cm^{-1} for $\delta_{\sigma' a}$ is obtained by means of (160f)[5].

It is seen that the agreement between the observed and the calculated frequencies in these molecules is satisfactory in general.[6]

2) C_2Cl_4

The infrared spectrum of tetrachlorethylene C_2Cl_4 has been studied by Wu[1] and the depolarization of the Raman lines by a few authors[2]. The infrared spectrum shows 3 intense bands at 702, 802 and 913 cm^{-1} and a weaker one at 755 cm^{-1} in the region from 1 to 22μ. The Raman spectrum shows 3 intense and partially depolarized lines at 234, 447 and 1570 cm^{-1}, and two weaker and completely depolarized lines at 341 and 512 cm^{-1}, and a very weak line at 383 cm^{-1} whose degree of depolarization cannot be accurately determined.[2] The comparative scarcity of absorption bands and Raman lines indicates a highly symmetrical structure, and the absence of infrared active frequencies in the Raman spectrum and vice versa shows that the molcule has a center of symmetry. The structure is hence like that of C_2H_4 and the following assignments can be made: The 3 polarized Raman lines are probably due to the 3 totally symmetrical vibrations $\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$, and the three weak lines to $\nu_{\sigma s}$, $\delta_{\sigma s}$, $\delta_{\sigma' s}$. The assignments of the infrared active fundamentals cannot be definitely given, since the region below 450 cm^{-1} has not been studied and some of the fundamentals certainly lie in this region. It is probable that the intense band at 913 cm^{-1} corresponds to $\nu_{\pi a}$. By means of (157), it is possible to estimate the frequency of $\delta_{\pi a}$ at *ca.* 345 cm^{-1}. Concerning the other fundamentals, little can be said from the data available at present.

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[5] Sutherland and Conn, *loc. cit.*, gave the value 505 cm^{-1} for $\delta_{\sigma' a}$ according to the potential (158). Application of (160f) shows, however, that this should be 719 cm^{-1} irrespective of the values of the potential constants h and Ω. In fact, the relation for $\delta_{\sigma' s}$ and $\delta_{\sigma' a}$ given by Sutherland and Dennison, Proc. Roy. Soc. A 148, 250, (1935), is equivalent to (160e) and (160f) for $\Omega \doteq 0$.

[6] Y. L. Chang, quoted in M. de Hemptinne *et al, loc. cit.*, has made corrections for anharmonicity in the calculations.

[1] T. Y. Wu, Phys. Rev. 46, 465, (1934).

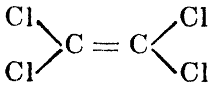
[2] L. Simons, Soc. Sci. Fenn. Comm. Phys. Math. 6, no. 13, (1932); T. Y. Wu, Jour. Chin. Chem. Soc. 5, 402, (1936); F. Heidenreich, Zeits. f. Physik 97, 277, (1935), studied the polarization of the Raman lines by means of circularly polarized light (see footnote 7 at end of section 6, Chap. II), and found the 383 cm^{-1} line to be "richtig". As the line is so weak and as it is measured only once, the result may be doubtful.

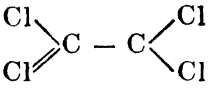
On the above assignments of the 5 frequencies $\nu_{\pi s}$, $\delta_{\pi s}$. $\nu_{2\pi s}$, $\nu_{\pi a}$, $\delta_{\pi a}$, it is possible to calculate some of the constants in the potentials (155), (158) and (161). Duchesne[3] has calculated the constants in a valence force potential given by Delfosse, and Thompson and Linnett[4] have employed a potential which is slightly different from (161). Their results are given below.

Constants	Duchesne	Thompson-Linnett	Potential (155)	Duchesne[5]
K_{CC}	6.25	6.18	6.81	~8
$k_{CCl}+k_2$	4.48	4.9		
a			4.70	
b			1.94	
d			1.62	
e			0.29	

Table LXVII. Potential constants of C_2Cl_4

From the low value for the C—C bond constant compared with the value 9.8×10^5 in C_2H_4, Duchesne and Thompson and Linnett concluded that this may indicate resonance between the following structures





While such a resonance is possible, it must be remembered that the calculations of the potential constants are based on an assignment of the fundamentals which is not completely definite.. One should perhaps accept all values for the potential constants with reserve until more definite informations concerning the fundamentals are available.[5]

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[3] J. Duchesne, Nature 139, 288, 634, (1937).

[4] H. W. Thompson & J. W. Linnett, Jour. Chem. Soc. Lond. P. 1393, (1937).

[5] That these 5 frequencies lead to a value for the C—C bond constant markedly different from that in C_2H_4 was first observed by Wu, Phys. Rev. 46, 465, (1934), who attributed the difference to the very approximate nature of the calculation and the incomplete knowledge concerning the frequencies of these vibrations. Duchesne has shown in a recent note, Nature 142, 256, (1938), that the C—C bond constant is in fact quite sensitive to the frequencies of these vibrations, and that using the 388 cm^{-1} Raman frequency instead of the 235 cm^{-1} for one of the totally symmetrical vibrations brings the C-C constant to *ca.* 8×10^5.

5) N_2O_4

The infrared and the Raman spectra of N_2O_4 have been studied by Sutherland[1] and the infrared spectrum also by Harris and King.[2] The scarcity of absorption bands and Raman lines indicates a structure possessing high symmetry. Sutherland assumed for the molecule the symmetry V_h as for C_2H_4. According to the selection rules in Table LXIII, the assignments of the observed frequencies are as follows.

Raman	Infra.		Assignments	
	(1)	(2)	V_h	V_d
1360	—		$\nu\pi s$	$\nu\pi s$
813	—		$\delta\pi s$	$\delta\pi s$
283	—		$\nu 2\pi s$	$\nu 2\pi s$
—	1265		$\nu\pi a$	$\nu\pi a$
—	752		$\delta\pi a$	$\delta\pi a$
1724 *w*	—		$\nu\sigma s$	$\nu_\sigma(2) = 1744$
500 *w*	—		$\delta\sigma s$	
—	1749		$\nu\sigma a$	
—	380		$\delta\sigma a$	$\delta_{\sigma'}(2) = 380$
?	—		$\delta\sigma' s$	
—	680		$\delta\sigma' a$	$\delta_\sigma(2) = 680$
—	—		δ	
	880		$\delta\sigma a + \delta\sigma s$	
	948		$\delta\sigma' a + \nu 2\pi s$	
	2060		$\nu\pi a + \delta\sigma s$	
	2620	2649	$\nu\pi a + \nu\pi s$	
		2967	$\nu\pi a + \nu\sigma s$	
		3077		
		3091	$\nu\sigma a + \delta\pi s$	
		3478	$\nu\sigma a + \nu\sigma s$	$2\nu_\sigma$
		3861 *w*	$\nu\pi a + 2\nu\pi s$	
		4160	$\nu\sigma a + 2\nu\pi a$	
		4230	$\nu\pi a + \nu\pi s + \nu\sigma s$	
		4340 *w*	$\nu\sigma a + 2\nu\pi s$	
		4478 *w*		
		4620 *w*	$\nu\pi a + 2\nu\sigma s$	
		4706 *w*	$\nu\pi a + 2\nu\sigma a$?	$2\nu\sigma + \nu\pi a$
		4778	$\nu\sigma a + \nu\sigma s + \nu\pi s$?	
		5197	$3\nu\sigma a$?	$3\nu\sigma$

Table LXVIII. Vibrational spectrum of N_2O_4

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[1] G. B. B. M. Sutherland, Proc. Roy. Soc. A 141, 342; 535, (1933).

[2] L. Harris & G. W. King, Jour. Chem. Phys. 2, 51, (1934). The bands observed by these authors are given in the third column. The 380, 880 cm^{-1} bands were observed by J. Strong and S. C. Woo, Phys. Rev. 42, 267, (1932).

According to Harris and King, however, the infrared and the Raman spectra do not exclude the possibility of a structure having the symmetry V_d, *i.e.*, one in which the planes of the two NO_2 groups are at right angles with each other. In this model, the three pairs of vibrations $(\nu_{\sigma s}, \nu_{\sigma a})$, $(\delta_{\sigma s}, \delta_{\sigma a})$, $(\delta_{\sigma' s}, \delta_{\sigma' a})$ become three doubly degenerate vibrations that are active in both absorption and the Raman effect. That the observed Raman lines do not coincide with the infrared frequencies may be due to the fact that the Raman spectrum is observed at liquid air temperature and in the solid the N_2O_4 molecules are known to be planar from X-ray studies.[3] It is possible that in gaseous N_2O_4, both the planar and the perpendicular forms are existent. It would be desirable to examine the infrared bands, especially the 680, 752 and 380 cm^{-1} bands, under higher resolution to enable a distinction into the A, B, and C type bands of an asymmetrical rotator for the planar model, or the parallel and perpendicular type bands of a symmetrical rotator for the V_d model.

For either the planar or the V_d model, the potential (155) can be applied. The constants calcclated from the observed frequencies are

$$c = k_{NN} = 1.50, \quad a = 6.87, \quad b = 4.54, \quad d = \pm\ 2.64 \qquad (167)$$

for e assumed to be zero. The loose binding of the two NO_2 groups is reflected in the low value of the N—N bond constant.

C) Plane $Z_2Y_2X_2$ Molecules with Symmetries C_{2h} and C_{2v}.

To these symmetry classes belong the *cis* and the *trans* isomers of dichloroethylene, dibromoethylene, etc. The selection rules for both types of molecules have been given in Table LXV in connection with the *cis* and *trans* dideuteroethylenes. The normal vibrations have not been treated because of the large number of constants in the potential for such a molecule as the *cis* $C_2H_2Cl_2$, while for the classification of the observed frequencies some approximate considerations are sufficient, as we shall see below.

1) *trans* $C_2H_2Cl_2$, 2) *cis* $C_2H_2Cl_2$

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[3] S. B. Hendrick, Zeits. f. Physik 70, 699, (1931).

[2] W. F. Giauque & J. D. Kemp, Jour. Chem. Phys. 6, 40, (1938), found fair agreement between the observed entropy and that calculated on assuming the V_d model with $\delta_\sigma(2) = 382$, $\delta_{\sigma'}(2) = 500$ cm^{-1}. This is however not conclusive evidence against the planar model, since the same agreement will be obtained on the basis of the assignments in Table LXVIII for the planar model.

The Raman spectra of these molecules have been studied by Bonino and Brüll[1], and the degrees of depolarization by Trumpy[2], Heidenreich[3], Paulsen[4] and Cabannes[5]. The infrared absorption spectra of these isomers have been investigated in the region $2-22\mu$ by Wu.[6] Paulsen and Cabannes treated these molecules as 4 -particle systems X$-$(CH)$-$(CH)$-$X possessing 6 fundamentals. It has been shown by Wu,[7] however, that a satisfactory correlation of the observed infrared and the Raman frequencies with the 12 modes of vibrations in each molecule can be made by considering it as made up of two CHX groups. Thus in *trans* $C_2H_2Cl_2$, the three pairs of observed frequencies

$$\begin{cases} 840 \text{ Ra.} \\ 820 \text{ Inf.} \end{cases} \qquad \begin{cases} 1270 \text{ Ra.} \\ 1200 \text{ Inf.} \end{cases} \qquad \begin{cases} 3072 \text{ Ra.} \\ 3090 \text{ Inf.} \end{cases}$$

can be ascribed to the vibrations ν_1, ν_2, ν_3 respectively in the CHCl group, the difference in each pair being due to the coupling of the two CHCl groups. With these frequencies, the constants in the simple valence force potential (20), Chap. II, can be calculated to be

$$k_{CH} = 5.17\times10^5, \quad k_{CCl} = 4.01\times10^5, \quad k_\alpha = 1.71\times10^{-11}, \qquad (168)$$

With these constants, equations (21), Chap. II, give for CDCl the frequencies

$$\nu_1 = 755, \qquad \nu_2 = 960, \qquad \nu_3 = 2320 \text{ cm}^{-1}. \qquad (169)$$

In fact, the frequencies 765, 992 and 2325 cm^{-1} are observed in the Raman spectrum of *trans* $C_2D_2Cl_2$. The closeness between the calculated frequencies for CDCl and the observed ones for $C_2D_2Cl_2$ shows (*i*) that the CHCl or CDCl groups retain a large part of their identity in the molecules $C_2H_2Cl_2$ or $C_2D_2Cl_2$, and (*ii*) that the building up of the fundamental vibrations of these molecules from those of the CHCl groups and the subsequent assignments are justified. In Tables LXIX and LXX are given the assignments of the infrared and Raman frequencies of *trans* and *cis* $C_2H_2Cl_2$ and $C_2D_2Cl_2$ according to Wu, the notations for the vibrations being those employed for C_2H_4 for convenient comparisons with Fig. 35.

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[1] Bonino & Brüll, Zeits. f. Physik 58, 194, (1929); Atti. Accad. Lincei 13, 275, (1931).

[2] B. Trumpy, Zeits. f. Physik 90, 133, (1934); 98, 672, (1935).

[3] F. Heidenreich, *ibid.*, 97, 277, (1935).

[4] Paulsen, Zeits. f. phys. Chem. B 28, 123, (1935).

[5] J. Cabannes, Jour. de Chim. Phys. 35, 1, (1938).

[6] T. Y. Wu, Phys. Rev. 46, 465, (1934); G. Emschwiller & J. Lecomte, Jour. de Phys. et Rad. 8, 130, (1937), measured the absorption bands of the liquids between 525 and 1450 cm^{-1}. The frequencies obtained are in approximate agreement with those of Wu.

[7] T. Y. Wu, Jour. Chem. Phys. 5, 392, (1937).

Vibration	$C_2H_2Cl_2$ Infrared	$C_2H_2Cl_2$ Raman	ϱ	$C_2D_2Cl_2$ Raman
$\nu_{\pi s}$	—	840 (3)	0.08	765 (2)
$\delta_{\pi s}$	—	1270 (7)	0.20	992 (6)
$\nu_{2\pi 3}$	—	1575 (5)	0.08	1570 (6)
$\nu_{\pi a}$	820	—		—
$\delta_{\pi a}$	1200	—		—
$\nu_{\sigma s}$	—	3072 (5)	0.20	2325 (4)
$\delta_{\sigma s}$	—	350(10)	0.29	346 (4)
$\nu_{\sigma a}$	3090	—		—
$\delta_{\sigma a}$	?	—		—
$\delta_{\sigma' s}$	—	752 (2)	0.70	657 (1)
$\delta_{\sigma' a}$	620	—		—
δ	917	—		—
$\delta_{\pi s}+\delta_{\sigma s}$		1625 (¼)	p	1323 (0)
$2\nu_{\pi 3}$		1690 (½)	p	1540 (3)
$2\nu_{3\pi 3}$		3140 (½)	p	3150 (0)

Table LXIX. Vibrational spectra of *trans* $C_2H_2Cl_2$ & $C_2D_2Cl_2$.

Vibration	$C_2H_2Cl_2$ Infrared	$C_2H_2Cl_2$ Raman	ϱ	$C_2D_2Cl_2$ Raman
$\nu_{\pi s}$	711 *B*	711 (7)	0.07	689 (6)
$\delta_{\pi s}$	1181 ?	1180 (5)	0.70	850 (3)
$\nu_{2\pi s}$	1591 *B*	1586 (7)	0.08	1575 (6)
$\nu_{\pi a}$	857 *A*	?		?
$\delta_{\pi a}$	1303 *A*	?		?
$\nu_{\sigma s}$	3087 *B*	3078(10)	0.31	2325 (6)
$\delta_{\sigma s}$	?	174 (9)	0.50	171 (6)
$\nu_{\sigma a}$	?	?		?
$\delta_{\sigma s}$	?	407 (5)	0.84	368 (3)
$\delta_{\sigma' s}$	—	806 (¼)	d	?
$\delta_{\sigma' a}$	694 *C*	—		—
torsion	—	878 (½)	p?	?
?	570 *B*	560 (2)	0.88	515 (1)
?		1688 (2)	p?	1507 (2)
$2\nu_{2\pi s}$		3158 (½)	p?	3150 (0)

Table LXX. Vibrational spectra of *cis* $C_2H_2Cl_2$ & $C_2D_2Cl_2$

In Tables LXIX and LXX, there are a few low frequency fundamentals that have not been observed in the infrared study of Wu. Recently, Yeou[8] has measured the absorptions of the liquid *trans* and *cis* $C_2H_2Cl_2$ between 6000 and 9300 cm^{-1} and found a number of bands that he ascribed to the harmonics $2\nu(CH)$ and $3\nu(CH)$ of a C−H fundamental and the combinations of $2\nu(CH)$ with the other fundamentals. The following table gives the frequency differences between these combination bands and the band at 6050 cm^{-1} in each molecule, together with the corresponding fundamentals in Tables LXIX and LXX that enter into the combinations.

Trans $C_2H_2Cl_2$ Obs. bands			Assign.	*Cis* $C_2H_2Cl_2$ Obs. bands			Assign.
6048 + 179			$2\nu_{OH}+\delta_{\sigma a}$	6050 + 100			$2\nu_{\sigma a}, 2\nu_{\sigma s}, \nu_{\sigma a}+\nu_{\sigma s}$
273	*w*			192		(174)	$+\delta_{\sigma s}$
342	*w*	(350)	$\nu_{\sigma a}+\nu_{\sigma s}+\delta_{\sigma s}$	259	*w*		
575		(620)	$2\nu_{\sigma s}+\delta_{\sigma' a}$	393		(407)	$+\delta_{\sigma a}$
672	*w*			568	*w*	(570)	
745		(752)	$\nu_{\sigma a}+\nu_{\sigma s}+\delta_{\sigma' s}$	675		(694)	$+\delta_{\sigma' a}$
852		(820)	$2\nu_{\sigma s}+\nu_{\pi a}$	845		(857)	$+\nu_{\pi a}$
877		(840)	$\nu_{\sigma a}+\nu_{\sigma s}+\nu_{\pi s}$	943	*w*		
974	*w*	(917)	$2\nu_{\sigma s}+\delta$	1012	*w*		
1183		(1200)	$2\nu_{\sigma s}+\delta_{\pi a}$	1093	*w*		
1257		(1270)	$\nu_{\sigma a}+\nu_{\sigma s}+\delta_{\pi s}$	1165		(1180)	$+\delta_{\pi s}$
1580		(1575)	$\nu_{\sigma a}+\nu_{\sigma s}+\nu_{2\pi s}$	1281		(1303)	$+\delta_{\pi a}$
				1595		(1591)	$+\nu_{2\pi s}$

Table LXXI. Combination bands in *trans* & *cis* $C_2H_2Cl_2$

An assignment is given each band, which in the case of the *cis* $C_2H_2Cl_2$ cannot be completely definite because of the 3 possibilities $\nu_{\sigma a}+\nu_{\sigma s}$, $2\nu_{\sigma s}$, $2\nu_{\sigma a}$ for the band at 6050 cm^{-1}. It is seen from Table LXXI that when due consideration is given to the effect of the anharmonicity of vibrations, these combination bands establish the fundamental frequencies given in Tables LXIX and LXX.

Concerning the potentials of the *cis* and *trans* $C_2H_2Cl_2$, very little can be said, except that the HCCl groups retain considerable parts of their identity in these molecules and have potential functions approximately given by (168). An interesting question concerning these isomers is that of their relative stabilities. Ebert and Büll determined the equilibrium ratio of the two isomers at 300°C and found 63% of the *cis* and 37% of the *trans* form.[9] This at first seems to indicate a greater stability for the *cis* form,[10] in contradication with other known isomers. It has been shown by Altar,[11] however, that a statistical calculation of the equilibrium ratio of *cis* to *trans* form from their moments of inertia turns out to be 62.3: 37.7 even in the absence of any difference in the stability of the two forms. On the basis of this calculation, the observed equilibrium ratio does not necessarily mean a greater stability for the *cis* form, but can be understood if the two forms have approximately the same energy of formation, as shown by Altar from a calculation of the interaction of the two groups.

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[8] Yeou Ta, C. R. 207, 326, (1938). The 6048 cm^{-1} band of *trans* $C_2H_2Cl_2$ was given as 2ν (CH). This needs a slight modification, as shown in Table LXXI, as no odd harmonics of any fundamental are active in absorption since the *trans* isomer possesses a symmetry center.

3, 4, 5, 6) *Cis* and *trans* $C_2H_2Br_2$ and $C_2H_2I_2$

The infrared and the Raman spectra of these molecules have been studied by Emschwiller and Lecomte[1]. The data are incomplete for the

	$C_2H_2Cl_2$		$C_2H_2Br_2$		$C_2H_2I_2$	
	Infra.	Ram.	Infra.	Ram.	Infra.	Ram.
$\nu_{\pi s}$	711	711	579	580		
$\delta_{\pi s}$	1181	1180		1150	1094 ?	
$\nu_{2\pi s}$	1591	1586	1547	1584		
$\nu_{\pi a}$	857		673		586	
$\delta_{\pi a}$	1303		1229		1163 ?	
$\nu_{\sigma s}$	3087	3708	(3000)	3084	(3000)	
$\delta_{\sigma s}$		174		109		
$\nu_{\sigma a}$	(3000)		(3000)		(3000)	
$\delta_{\sigma a}$		407		372		
$\delta_{\sigma' s}$	—	806	—		—	
$\delta_{\sigma' a}$	694	—		—	653	—
δ	—	878	—		—	

Table LXXII. Fundamental frequencies of *cis* $C_2H_2Br_2$ & $C_2H_2I_2$

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[9] Ebert and Büll, Zeits. f. phys. Chem. A 152, 451, (1931).

[10] H. A. Stuart, *Molekülstruktur*, P. 95, (1934).

[11] W. Altar, Jour. Chem. Phys. 3, 460, (1935).

[1] G. Emschwiller & J. Lecomte, Jour. de Phys. et Rad. 8, 130, (1937), gave the following infrared frequencies for *cis* and *trans* $C_2H_2Br_2$: 579, 673, 746, 829, 896, 1028, 1145, 1229, 1334 and 1547 cm^{-1}; the infrared frequencies for *cis* $C_2H_2I_2$: 586, 653, 730, 905, 1094, 1163 and 1448 cm^{-1}; for *trans* $C_2H_2I_2$: 588, 664, 704, 730, 895, 1051 and 1120 cm^{-1}. Also Kohlrausch, Der Smekal-Raman Effekt, P. 326.

assignments of all the fundamental frequencies in these molecules, as the infrared work covers only the spectral region 525–1450 cm^{-1} and the Raman lines in the region 3000 cm^{-1} are not given. Furthermore, in the absence of Raman effect data for both the *cis* and *trans* $C_2H_2I_2$, polarization measurements for the $C_2H_2Br_2$ isomers, and separate infrared data for the two isomers of $C_2H_2Br_2$, we can give only a tentative classification which is based on a comparison with the $C_2H_2Cl_2$ molecules.[2]

	$C_2H_2Cl_2$ Infra.	$C_2H_2Cl_2$ Ram.	$C_2H_2Br_2$ Infra.	$C_2H_2Br_2$ Ram.	$C_2H_2I_2$ Infra.	$C_2H_2I_2$ Ram.
$\nu_{\pi s}$	—	840	—	748	—	
$\delta_{\pi s}$	—	1270	—	1246	—	
$\nu_{2\pi s}$	—	1575	—	578	—	
$\nu_{\pi a}$	820	—	746	—	664	—
$\delta_{\pi a}$	1200	—	1145?	—	1051	—
$\nu_{\sigma s}$	—	3072	—	3084	—	
$\delta_{\sigma s}$	—	350	—	218	—	
$\nu_{\sigma a}$	(3090)	—		—		—
$\delta_{\sigma a}$	(179)	—		—		—
$\delta_{\sigma' s}$	—	752	—	453	—	
$\delta_{\sigma' a}$	620	—		—		—
δ	917	—		—		—

Table LXXIII. Fundamental frequencies of *trans* $C_2H_2Br_2$ & $C_2H_2I_2$

Further work on the infrared and the Raman spectra of these dihalogen derivatives of ethylene, especially polarization measurements, is desirable in order to complete the systematics of the spectra of these molecules.

7) Asymmetrical $F_2C=CCl_2$

The Raman spectrum of this molecule in the liquid state has been measured by Hatcher and Yost[1] who found 11 lines. The selection rules for the normal vibrations is given in Table LXV. There should be 5 polarized and 4 depolarized lines in the Raman spectrum. In the absence of polarization data, we can only make the following tentative assignments.

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[2] It is apparent that not all the observed bands of Emschwiller and Lecomte, *loc. cit.*, can be fundamentals, but the lack of the low frequency fundamentals makes any assignment of them as harmonic and combination bands quite uncertain. They ascribed certain bands to 2ν's of the *trans* isomers, each molecule being regarded as a 4-particle system X–(CH)–(CH)–X. But in the trans isomer possessing a symmetry center, no odd harmonics of any fundamental should be active in the infrared.

In the group of 5 totally symmetrical vibrations, one is roughly the symmetrical valence vibration ν_1 in CF_2, one a similar vibration in CCl_2, one a deformation vibration ν_2 in CF_2, one a similar one in CCl_2, and the last a vibration in the C=C bond. To these may be assigned the intense lines 1027(2), 435(7), 562(6), 235(6) and 1735(6) respectively. Of the 4 antisymmetrical (planar) vibrations, one is roughly the antisymmetrical valence vibration ν_3 in CF_2, one a similar one in CCl_2, and the other two are deformation vibrations in the CF_2 and CCl_2 groups about the symmetry axis in the plane of the molecule. To these may be assigned the lines 1123(1), 622(4), 648(2) and 454(1) respectively. Of the other 3 vibrations, two are deformation vibrations of the CF_2 and CCl_2 groups perpendicular to the plane of molecule and one is a torsional vibration of the two groups about the C=C axis. These frequencies do not seem to have been represented in the Raman spectrum. A weak line observed at 883(½) may be the harmonic of the 435 cm^{-1} fundamental, or the combination 435+454. Another weak line at 1976(½) may be the combination 1735+235 or 1123+883. A final assignment can only be made when polarization data are available.

D) Axially Symmetrical $TZYX_3$ Molecule

Molecules of this type are H_3C-CN and H_3C-NC. There are four totally symmetrical and four doubly degenerate vibrations. Of the symmetrical vibrations, one is roughly the valence vibration ν_1 in CH_3, one the deformation vibration ν_3 in CH_3, and the other two are the valence vibrations in the C−C and C≡N bonds. Of the degenerate vibrations, one involves the valence vibration ν_2 in CH_3, one the deformation vibration ν_4 in CH_3, and the other two are roughly the perpendicular vibrations of the 4-particle system $(H_3)-C-C-N$ or $(H_3)-C-N-C$. The selection rules of these vibrations are as follows: The symmetrical vibrations give rise to polarized Raman lines and the parallel type absorption bands, and the degenerate vibrations to depolarized Raman lines and perpendicular type bands.

A normal coordinate treatment can readily be given for the symmetrical vibrations. With the modified valence force potential

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[1] J. B. Hatcher & D. M. Yost, Jour. Chem. Phys. 5, 992, (1937).

$$2V = 3k(\delta r)^2 + 3k_\Theta (r\delta\Theta)^2 + 3k_\varphi (s\delta\varphi)^2 + k_1 (\delta R_1)^2 + k_2 (\delta R_2)^2 + 6k_3 (s\delta\varphi)\,\delta R_1 + 2k_4 (\delta R_1)(\delta R_2), \tag{170}$$

where r, R_1, R_2 are the X−Y, Y−Z, Z−T distances, Θ and φ the X−Y−X and X−Y−Z bond angles, respectively, the determinantal equation is

$$\begin{vmatrix} A\lambda - k & C\lambda & F\cos\varphi\,\lambda & G\cos\varphi\,\lambda \\ C\lambda & B\lambda - k_\alpha & -(F\sin\varphi\,\lambda - k_3) & -G\sin\varphi\,\lambda \\ 3F\cos\varphi\,\lambda & -3(F\sin\varphi\,\lambda - k_3) & (D\lambda - k_1) & H\lambda - k_4 \\ 3G\cos\varphi\,\lambda & -3G\sin\varphi\,\lambda & H\lambda - k_4 & E\lambda - k_2 \end{vmatrix} = 0, \tag{171}$$

where

$$AS = m(M + M_1 + M_2 + 3m\sin^2\varphi), \qquad BS = m(M + M_1 + M_2 + 3m\cos^2\varphi),$$
$$CS = 3m^2 \,|\cos\varphi\,|\sin\varphi\,, \qquad DS = (M + 3m)(M_1 + M_2),$$
$$ES = M_2(M + M_1 + 3m)\,, \qquad FS = m(M_1 + M_2), \qquad GS = mM_2,$$
$$HS = M_2(M + 3m)\,, \qquad S = M + M_1 + M_2 + 3m\,,$$
$$k_\alpha = k_\varphi + k_\Theta \left(\frac{r}{s}\right)^2 \frac{12\cos^2\varphi}{1 + 3\cos^2\varphi}\,.$$

1) H_3C-CN (methyl cyanide), 2) H_3C-NC (methyl isocyanide)

The Raman spectra of H_3C-CN and H_3C-NC have been studied by a number of authors.[1] On the above considerations of the approximate nature of the normal vibrations, the following assignments can be made, although the frequencies given for the perpendicular vibration in these molecules may be uncertain.

	H_8C-CN	H_8C-NC	
ν_1 (ν_1 in CH_8)	2942(10)	2951(6)	
ν_2 (ν_8 in CH_3)	1370(3b)	1414(3)	
ν_8 (C—C;C—N)	917 (3)	928(3)	
ν_4 (C≡N)	2250 (6)	2161(6)	(172)
ν_5 (ν_2 in CH_8)	2996 (1)	3002(1)	
ν_6 (ν_4 in CH_8)	1417 (½)	1456(1)	
ν_7	1125 (¼)	1041(1)	
ν_8	376 (4)	290(5)	

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[1] Kohlrausch, *Der Smekal-Raman Effekt;* A. W. Reitz & R. Skrabal, Monatshefte f. Chem. 70, 398, (1937).

With the 4 parallel frequencies in each molecule, it is possible to determine the 4 constants k, k_α, k_1, k_2 from (171) by neglecting k_3, and k_4. The values so obtained are:

(*i*) for H_3C-CN,

$$k = 4.9\,,\qquad k_\alpha = 0.92\,,\qquad k_1 = 5.2\,,\qquad k_2 = 17.0;$$

(*ii*) for H_3C-NC,

$$k = 4.9\,,\qquad k_\alpha = 0.92\,,\qquad k_1 = 5.7\,,\qquad k_2 = 16.0\,.$$

It is seen that the $C\equiv N$ bond is stronger in cyanide than in isocyanide, in agreement with the observations on HCN and HNC (see §1, A, 5).

E) Molecules Possessing No Symmetries

1) CH_3OH (methyl alcohol), 1a) CH_3OD, 1b) CH_2DOD

The structure of the methyl alochol molecule is one in which the oxygen atom takes the place of the halogen atom in the methyl halides, the H atom in the hydroxyl OH group being off the $C-O$ axis. As the single bond $C-O$ has no directional properties, the potential energy of the molecule as a function of the orientation of the $O-H$ bond about the $C-O$ axis will depend on the interaction between the H atom in $O-H$ and the H atoms in the methyl group and will possess 3 identical minima and 3 maxima in 2π. Whether the $O-H$ group oscillates about one of 3 positions of minimum energy or rotates freely about the $C-O$ axis is determined by the height of the potential barriers. A study of the spectrum of the molecule will throw light on this question.

Because of the small mass of the hydrogen atom in the $O-H$ group, the CH_3OH molecule will behave very much like an axially symmetrical molecule in its normal vibrations. Disregarding the H atom in the $O-H$ group, one has the CH_3O group which possesses 3 parallel vibrations ν_1, ν_3, ν_5 and 3 doubly degenerate vibrations ν_2, ν_4, ν_6. The nature of these vibrations and their modes have been discussed in §3,C and shown in Fig. 32. On including the H atom of the $O-H$ group, one obtains 3 more vibrations: ν_7 for the valence vibration of $O-H$, ν_8 for the above mentioned oscillation or rotation of $O-H$ bond about the $C-O$ axis, and ν_9 for the deformation of the $H-O-C$ bond angle.

Similar considerations hold for the CH_3OD and the CH_2DOD molecules, except that the greater departure from axial symmetry on account of the greater mass of the D atoms in these molecules may bring about a splitting of the "doubly degenerate" vibrations ν_2, ν_4, ν_6.

The Raman and the infrared spectra of these molecules have been studied by a number of authors[1,2]. The observed frequencies and their assignments are given below.

Vibration	CH_3OH		CH_3OD		CH_2DOD	
	Raman	Infra.	Raman	Infra.	Raman	Infra.
ν_7(O-H),(O−D)	3382	3683	2494	2720	2501	2718.8
ν_2	2987(5)	2978	2987(6)	2965	2979(5)	2944
ν_1, $2\nu_4$	2942(9)p		2946(10)		2948(10)	
$\nu_3+\nu_4$	2913(5)		2017(5)			
ν_1, $2\nu_4$	2837(1)p	2845	2836(9)	2850	2882(9)	2874
					2835(3)	
					2683(3)	
	2588(1)		2591(1)			
						2158.4
					2237 ?	
ν_{2-2}					2175(6)	2180
$2\nu_5$		2054		2065		
ν_4	1464(5)d	1477		1480	1469(5)	
ν_3	1451(4)	1455	1464	1459	1343(5)	1357
ν_6	1370 ?	1340				
ν_{4-7}					1301(6)	1330
			1226(1)			
	1153(1)		1154(2)			
	1110(2)		942(2)	863		952.9
ν_9					894(2)	892.3
						829.5
						810.1
ν_5(O−C)	1029(6)p	1034.18	1031(5)	1040	1037(7)	1049. Q
						1023. Q
		380−860				
ν_8						ca.16 μ

Table LXXIV. Vibrational spectra of CH_3OH, CH_3OD & CH_2DOD.

The following remarks will make the table clear.

(i) It is seen that the frequencies ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, the first 4 being characteristic of the methyl group and the last 2 of H_3CO, remain more or less the same in these molecules.

(ii) The presence of two intense Raman lines at *ca.* 2945 & 2840 cm^{-1} in each of these molecules is due to the resonance interaction between

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[1] J. O. Halford, L. C. Anderson & G. H. Kissen, Jour. Chem. Phys. 5, 927, (1937); Mizushima, Morino & Okamoto, Bull. Chem. Soc. Jap. 11, 698, (1936); polarization data on CH_3OH from J. Wagner, Zeits. f. phys. Chem. B 40, 36, (1938).

[2] Infrared: A. Borden & E. F. Barker, Jour. Chem. Phys. 6, 553, (1938); Barker & G. Bosschieter, *ibid.*, 6, 563, (1938); Bosschieter, *ibid.*, 5, 992, (1937).

ν_1 and $2\nu_4$ as in the methyl halides. That only one parallel band at about 2850 cm^{-1} is found in the infrared is due to the overlapping of the other band by the intense ν_2 band in these molecules.

(iii) The O-H frequency 3683 cm^{-1} of CH_3OH vapor shifts to 3382 cm^{-1} in the liquid, and the O-D frequency 2720 in CH_3OD vapor shifts to 2500 in the liquid. Such shifts are due to the association of the molecules in the liquid state as shown by Errera, Mollet and others for ethyl alcohol and other organic acids.[3]

(iv) In CH_3OH, a series of absorption lines extends from about 380 to 860 cm^{-1}, with spacings varying from ca. 10 cm^{-1} on the low frequency side to *ca.* 40 cm^{-1} on the high frequency side. This absorption region has been ascribed by Borden and Barker to ν_8. Approximate calculations show that if this is a pure oscillation, the band will be a perpendicular type band with a spacing of about 6.5 cm^{-1} between the Q branches; but if the O-H bond rotates freely about the C-O axis, there will then be a series of bands separated by about 40 cm^{-1} from one another. The explanation of the observed absorption region is perhaps as follows: the low frequency end is probably due to the oscillatory motion while the high frequency end is due to the more or less free rotation in the higher quantum states.

(v) The ν_5 band at 1034 cm^{-1} of CH_3OH has been completely resolved, the rotational lines being expressible by the expression:

$$\nu = 1034.18 \pm 1.5975\, m - 0.0088\, m^2.$$

From this and the dimensions of the CH_3 and OH groups found for CH_4 and H_2O, the following values for the greatest and the intermediate moments of inertia are obtained:

$$I_C = 35.18\,, \qquad I_B = 33.83 \times 10^{-40}\,\text{g.cm}^2.$$

The ν_5 band of CH_3OD has also been resolved, the rotational lines being given by the expression

$$\nu = 1040.6 \pm 1.58\, m - 0.008\, m^2.$$

From this, the average value of I_C and I_B was obtained as 35.0×10^{-40}.

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[3] See footnote (1), Chap. III, §5, B).

[4] Halford, Anderson & Kissen, *loc. cit.* The objection of Wagner, *loc. cit.*, against the assignment of the depolarized line 1464 cm^{-1} of CH_3OH to ν_3 by Halford *et al* is now removed by the assignments ν_8=1455 and ν_4=1477 cm^{-1} from the infrared data.

(vi) From the frequencies ν_1, ν_3, ν_5, it is possible to calculate the constants in the valence force potential (136) with $k_4=0$ for the H_3CO group. Assuming tetrahedral angles, the values of the constants are[4]

$$k_{CH} = 4.8\,, \qquad k_{CO} = 5.77\,, \qquad k_{\alpha}\,(s/r)^2 = 0.87 \qquad (171)$$

(vii) In CH_2DOD, the asymmetry caused by the D atom in the methyl group brings about the removal of the degeneracy in the vibrations ν_2, ν_4, ν_6. The extra frequencies are denoted by ν_{2-2}, ν_{4-2}, and ν_{6-2}.

§5. **Seven-atomic Molecules**

A) Octahedral YX_6 Molecules

A molecule with six identical atoms at the centers of the faces of a cube and another atom at the center of the cube possesses one single totally symmetrical vibration ν_1, one doubly degenerate vibration $\nu_2(2)$, and four tribly degenerate vibrations $\nu_3(3)$, $\nu_4(3)$, $\nu_5(3)$, $\nu_6(3)$. The general forms of the normal vibrations are shown in Fig. 36.

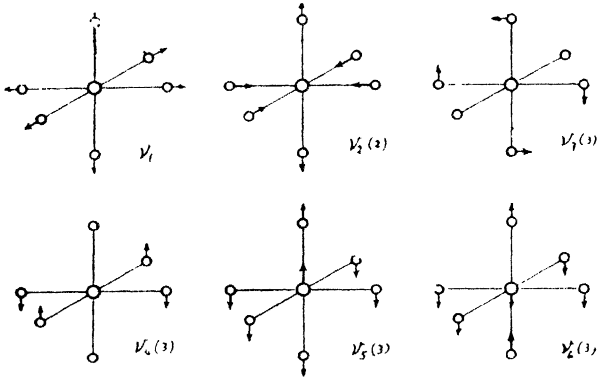

Fig. 36. Normal vibrations of octahedral YX_6 molecules. The actual forms of the vibrations ν_5 and ν_6 are combinations of the forms shown in the figure

The selection rules obtained on considerations of the symmetry properties are as follows:

	ν_1	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$	$\nu_5(3)$	$\nu_6(3)$
Infrared	ina.	inac.	ina.	ina.	act.	act.
Raman	p	d	d	ina.	ina.	ina.

The normal vibrations have been treated by Yost, Steffens and Gross[1] and by Wilson.[2] The last author employed a potential of the valence force type

$$2V = k\sum^{6}(\delta r_i)^2 + 2k_1\sum_{i\neq j}(\delta r_i)(\delta r_j) + k_\alpha\sum(r\delta\varphi_i)^2, \qquad (173)$$

where the second summation is taken over adjacent $r_i = Y-X_i$ bonds and φ is the $X-Y-X$ bond angle. The determinantal equation gives

$$m\lambda_1 = k + 4k_1, \qquad m\lambda_2 = k - 2k_1,$$

$$m\lambda_3 = 4k_\alpha, \qquad m\lambda_4 = 2k_\alpha,$$

$$m(\lambda_5 + \lambda_6) = \frac{2M}{3(M+4m)}\left[1 + \frac{4m}{M} + \frac{12m^2}{M^2}\right]k + \frac{8}{3}\left[\frac{M+3m}{M}\right]k_\alpha,$$

$$m^2\lambda_5\lambda_6 = \frac{4(M+6m)^2}{3M(M+4m)}kk_\alpha.$$

This simple potential is useful in that it can be determined from three of the normal vibrations, the Raman frequencies for example; but from our experience with such molecules as the tetrahalides of carbon, silicon, etc., we would hardly expect it to be more than qualitative when applied to the actual molecules.

1) SF_6, 2) SeF_6, 3) TeF_6

That these molecules have tetrahedral symmetry O_h is established by electron diffraction measurements.[3] The Raman spectra of these molecules have been studied by Yost, Steffens and Gross, and the infrared spectra by Eucken, Ahrens, Sachsse and Bartholomé.[4] The following table summarizes the observed data, the constants in (173) determined from ν_1, ν_2, ν_3, and the frequencies ν_4, ν_5, ν_6 calculated with these potential constants.

[1] Yost, Steffens & Gross, Jour. Chem. Phys. 2, 313, (1934).

[2] E. B. Wilson, Jr., quoted in the above paper.

[3] L. O. Brockway & L. Pauling, Proc. Nat. Acad. Sci. 19, 68, (1933).

[4] SF_6 from A. Eucken & H. Ahrens, Zeits. f. phys. Chem. B 26, 297, (1934); SeF_6 and TeF_6 from H. Sachsse & E. Bartholomé, *ibid.*, B 28, 257, (1935); Eucken & E. Sauter, *ibid.*, B 26, 463, (1934).

[5] These frequencies of SF_6 lead to a calculated entropy S(298°K) 69.24 cal/mole/degree in agreement with the thermal value 69.43, according to Eucken & E. Schröder, *ibid.*, B 41, 307, (1938)

	ν_1	ν_2	ν_3	ν_5	ν_6	ν_4	k	k_1	k_α
SF_6	772.4.(gas)			617	965				
	776 (liq)	642	525	(540)	(970)	(370)	5.30	0.34	0.77
SeF_6	708 (gas)			461	787				
	710 (liq)	662	405	(430)	(650)	(286)	5.15	0.12	0.46
TeF_6	701 (gas)	674	313	370	752				
	697 (liq)	672	316	(310)	(610)	(222)	5.23	0.09	0.27

Table LXXV. Fundamental frequencies & potential constants of SF_6, SeF_6, TeF_6. Calculated frequencies are in parentheses.

The bond distances are as follows:

$$r(\text{S}-\text{F}) = 1.57\ \text{Å}, \qquad r(\text{Se}-\text{F}) = 1.68\ \text{Å}, \qquad r(\text{Te}-\text{F}) = 1.83\ \text{Å}.$$

B) Y_3X_4 (symmetry V_d) Molecules

To this class belongs the allene molecule H_2CCCH_2. According to the theory of directed valence, the three C atoms would lie in a line with the planes of the two CH_2 groups at right angles with each other. The selection rules for the normal vibrations are as follows:

Vibrations	Symmetry	Infra.	Raman
$\nu_{\pi s}$, $\delta_{\pi s}$, $\nu_{2\pi s}$	A_1	ina.	p
$\nu_{\pi a}$, $\delta_{\pi a}$, $\nu_{2\pi a}$	B_2	$\mathfrak{M}_z$	d
$\nu\sigma(2)$, $\delta\sigma(2)$, $\delta'\sigma(2)$, $\delta''_\sigma(2)$	E	$\mathfrak{M}_x$, $\mathfrak{M}_y$	d
torsion	B_1	ina.	d

Table LXXVI. Selection rules for allene molecule

The nature of these vibrations can be roughly described as follows. Of the 3 totally symmetrical vibrations in class A_1, one can be pictured as a symmetrical valence vibration ν_1 in the CH_2 groups, one as a deformation vibration ν_2 in the CH_2 groups, and one as a vibration of the two CH_2 groups about the central C atom. The 3 vibrations in class B_2 differ from these only in the phase relation of the vibrations in the two CH_2 groups. Of the degenerate vibrations, one involves the valence vibration ν_8 in CH_2, and the other three are the perpendicular vibrations of the linear 5-atomic system (H_2)-C-C-C-(H_2) as shown in Fig. 30 for the carbon suboxide molecule.

The six vibrations in the classes A_1 and B_2 can be treated by the modified valence force potential

$$2V = k\sum^{4}(\delta r_i)^2 + k_1\sum^{2}(\delta R_i)^2 + k_\Theta\sum^{2}(r\delta\vartheta_i)^2 + k_\varphi\sum^{4}(s\delta\varphi_i)^2$$
$$+ 2k_2\,\delta R_1\,\delta R_2 + 2k_3\,r\,(\delta R_1\,\delta\theta_1 + \delta R_2\,\delta\theta_2), \qquad (174)$$

where the r's are the C–H distances, R's the C–C distances, θ's the H–C–H bond angles, and φ's the H–C–C angles. The frequencies of the totally symmetrical vibrations are given by[1]

$$\lambda_1+\lambda_2+\lambda_3 = \frac{1}{M}(k_1+k_2) + Qk + Nk_\alpha + Wk_3,$$
$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_1\lambda_3 = \frac{1}{mM}(k_1+k_2)(k+k_\alpha) + Ekk_\alpha + \frac{1}{m}Wkk_3 - \frac{2}{mM}k_3^2, \qquad (175a)$$
$$\lambda_1\lambda_2\lambda_3 = \frac{1}{m^2M}\,k\left[(k_1+k_2)\,k_\alpha - 2k_3^2\right],$$

and the antisymmetrical frequencies by

$$\lambda_4+\lambda_5+\lambda_6 = \frac{3}{M}(k_1+k_2) + Qk + Nk_\alpha + Wk_3,$$
$$\lambda_4\lambda_5+\lambda_5\lambda_6+\lambda_6\lambda_1 = \frac{1}{M}(Hk+Fk_\alpha)(k_1+k_2) + Ekk_\alpha + \frac{1}{m}Wkk_3 - \frac{2}{M}F\,k_3^2, \qquad (175b)$$
$$\lambda_4\lambda_5\lambda_6 = \frac{S}{m^2M^2}\left[(k_1+k_2)\,k_\alpha - 2k_3^2\right]k.$$

where

$$k_\alpha = 2k_\Theta + k_\varphi(s/r)^2, \quad Q = \frac{1}{m} + \frac{2}{M}\cos^2\frac{\theta}{2}, \quad N = \frac{1}{m} + \frac{2}{M}\sin^2\frac{\theta}{2},$$
$$F = 2N + \frac{1}{m}, \qquad H = 2Q + \frac{1}{m}, \qquad E = (M+2m)/Mm^2,$$
$$W = \frac{4}{M}\sin\frac{\theta}{2}, \qquad S = 3M + 4m.$$

The Raman spectrum of allene has been studied by a number of workers,[2] the infrared spectrum by Bonner and Hofstadter,[3] and both spectra more recently by Linnett and Avery.[4] The photographic region was examined by Eyster[5] who found 11 bands and partially resolved one of them at 8739 cm^{-1} into rotational lines. Their data and interpretations are summarized in Table LXXVII. The discrepancies between the infrared and the Raman frequencies are due to the fact that the infrared spectrum was observed for the vapor while the Raman spectrum was for the liquid. Because of the low dispersion in the infrared studies, the accuracy of the frequencies is not very high and it has not been possible

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[1] Equations (175a) have been given by H. W. Thompson and J. W. Linnett, Jour. Chem. Soc. London, P. 1384, (1937). Note the similarity between equations (175a), (175b) and (160a), 160b).

[2] Bourguel and Lespiaux, Bull. Soc. Chim. 51, 1041, (1932); Kopper and Pongratz, Wien. Ber. 141, 840, (1932).

[3] L. G. Bonner & R. Hofstadter, Phys. Rev. 52, 249, (1937).

[4] J. W. Linnett & W. H. Avery, Jour. Chem. Phys. 6, 686, (1938).

Assignment		Infrared	Raman
A_1	$\nu\pi s$	—	2992 (20)
	$\delta\pi s$	—	1430 (12)
	$\nu_2\pi s$	—	1069 (20)
B_2	$\nu\pi a$	broad band	(3000)
	$\delta\pi a$	1980 (10)	1956 (1)
	$\nu_2\pi a$	1389 (12)	?
E	$\nu\sigma(2)$	broad band	3062
	$\delta\sigma(2)$	1031 (8)	?
	$\delta'_\sigma(2)$	852 (30)	838 (5)
	$\delta''_\sigma(2)$	?	353 (4)
B_1	torsion δ	—	(820)
	$2\delta''_\sigma$		705 (2)
	$\delta + \delta''_\sigma$	1565 (1)	
	$2\delta'_\sigma$	1700 (8)	1684 (2)
	$\nu_2\pi a + \delta\sigma$	2420 (2)	
	$2\delta\pi s$		2858 (2)
	$\nu 2\pi a + 2\delta\pi s$	4200 (1)	
	$3\nu\pi a$	8738.96 ‖	
	$\nu\pi a + 2\nu\pi s$	8776.6 ‖	
		8722 ‖	
	$\nu\pi a + 2\nu\sigma$	8978 ‖	
	$\nu\pi s + 2\nu\sigma$	9012 ‖	
	$3\nu\sigma$	9076.7 ⊥	
		9718 vw	
		10420 ,,	
		11710 ,,	
	$3\nu\pi a + 2\nu_2\pi a, 3\nu\sigma + \nu_2\pi a + \delta\sigma$	11418 ‖, ‖	
	$5\nu\pi a$	13904 ‖	

Table LXXVII. Vibrational spectrum of allene to distinguish between the parallel and the perpendicular type bands from the band envelopes. The frequency 820 cm^{-1} given for the torsional vibration was estimated by Linnett and Avery from the specific heat data between 150 and 330°*K*. It is possible that the Raman line at 838 cm^{-1} may be due to a superposition of the two lines δ'_σ and δ.

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[5] E. H. Eyster, *ibid.*, 6, 580, (1938).

The C-C distance has recently been determined by electron diffraction measurements to be 1.34±0.02 Å.[6] From the rotational structure of the 8739 cm^{-1} band, Eyster obtained the value 97.0×10^{-40} $g.cm^2$ for the moment of inertia about an axis perpendicular to the C-C-C axis. On assuming the C-H distance to be 1.087Å obtained by an application of the Badger relation between bond force constant and bond distance (see below for force constant), and on assuming the value 5.67×10^{-40} $g.cm^2$ for the moment of inertia about the C−C−C axis found for C_2H_4 (165), he obtained the value 116° for the H−C−H bond angle and the value 1.33Å for the C−C distances. These values are in good agreement with the values in (166) given by Penney for the ethylene molecule.

With the six frequencies for the vibrations in the classes A_1 and B_2, the constants in the potential (174) can be determined,

$$k_2 + k_{CC} = 9.52, \qquad k_{CH} = 4.93,$$
$$k_\alpha = 2k_\Theta + k_\varphi (s/r)^2 = 1.17, \qquad k_3 = -0.58 \qquad (176)$$

the H−C−H bond angle being assumed to be 116°.

C) Axially Symmetrical Molecules

1) H_3C-C_2H (methyl acetylene)

This molecule possesses 5 parallel vibrations which are symmetrical with respect to the axis of symmetry, and 5 doubly degenerate vibrations. All the vibrations are active in absorption and in the Raman effect, the parallel vibrations being polarized and the degenerate vibrations depolarized. The modes of the vibrations may be roughly described as follows: Of the 5 parallel vibrations, one is the valence vibration ν_1 and one the deformation vibration ν_3 in the CH_3 group, one the C≡C vibration, one the C−C and the last the C−H vibration. Of the 5 degenerate vibrations, two involve the vibrations ν_2 and ν_4 of the CH_3 group (Fig. 26), and 3 are the perpendicular vibrations of the linear 5-particle system $(H_3)-C-C-C-H$ shown in Fig. 30.

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[6] L. Pauling & L. O. Brockway, Jour. Am. Chem. Soc. 59, 1223, (1937).

The Raman spectrum of methyl acetylene has been studied by Glockler, Davis and Wall.[1] No infrared data on the fundamentals seem to have been reported. Table LXXVIII summarizes the observed data and their interpretations.

Vibration		Liquid		Gas	
$\nu_\pi(C-H)$	ν_1	3305	(2*s*)	3306	
$\nu_\pi(CH_3)$	ν_2	2926	(10*s*)	2941	(10)
$2\delta_\sigma(CH_3)$		2867	(6*s*)		
$\nu_\pi(C\equiv C)$	ν_3	2123	(11*s*)	2142	(10)
$\delta_\pi(CH_3)$	ν_4	1382	(6*s*)	1420	?
$\nu_\pi(C-C)$	ν_5	929	(8*s*)	930	(5)
$\nu_\sigma(CH_3)$	ν_6	2971	(4*b*)		
$\delta_\sigma(CH_3)$	ν_7	1448	(2*b*)		
δ'_σ	ν_8	643	(5*b*)		
δ''_σ	ν_9	336	(9*b*)		
δ'''_σ	ν_{10}	?			
$2\delta_\pi$		2736	(1*b*)		

Table LXXVIII. Raman spectrum of methyl acetylene. *s*, sharp; *b*, broad.

The assignments of the 5 parallel fundamentals seem quite definite on considerations of their order of magnitudes. The appearance of the two lines at 2867 and 2926 cm^{-1} can be explained as the result of resonance interaction[2] between the parallel fundamental ν_2 and the first harmonic of the perpendicular fundamental ν_7.

Herzberg, Patat and Verleger[3] have analyzed a parallel type absorption band at 10304 Å (9700 cm^{-1}) by photographic techniques. From the rotational structure of the band, they obtained the value 1.463 Å for the C−C single bond distance, the assumption being made that the CH_3 group retains its dimensions as in CH_4 and the C≡C and C−H distances are the same as in C_2H_2. Badger and Bauer[4] obtained the same result from a partial analysis of a parallel type band at 9040 Å.

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[1] G. Glockler & H. M. Davis, Jour. Chem. Phys. 2, 881, (1934); Glockler & F. T. Wall, Phys. Rev. 51, 530, (1937), gaseous H_3C-C_2H. The line 1382 cm^{-1} was described as broad by Glockler and Davis, but from their microphotometer curve it appears to be as sharp as the other "s" lines.

[2] Cf. A. Adel & E. F. Barker, Jour. Chem. Phys. 2, 627, (1934); also R. M. Badger, *ibid.*, 5, 178, (1937).

[3] Herzberg, Patat & Verleger, Jour. Phys. Chem. 41, 123, (1937).

[4] R. M. Badger & S. H. Bauer, Jour. Chem. Phys. 5, 599, (1937).

Electron diffraction measurements give the values:[5] $r(C-C)=1.457$ Å, $r(C\equiv C)=1.198$ Å. The considerably smaller value for the C−C bond distance compared with the value 1.54 Å for normal single bond indicates constributions of double bond character arising from quantum mechanical reasonance.

The 5 parallel vibrations have been treated by Glockler and Wall[6] who employed a simple valence potential containing 5 constants, *viz.*, k_{C-H}, $k_{C\equiv C}$, k_{C-C}, and k_{C-H}, k_{α} for the CH_3 group. The determinantal equation is similar to (171) for the methyl cyanide and methyl isocyanide molecules. With the five parallel frequencies in Table LXXVIII, one obtains the following values

$$k_{C-H} = 4.75, \qquad k_{C\equiv C} = 14.5, \qquad k_{C-C} = 6.25,$$
$$k_{C-H} = 5.75, \qquad k_{\alpha} = 0.80\times 10^{5}.$$

These values are only approximate since the five frequencies do not suffice for the determination of interaction terms in the potential and since the anharmonicity corrections are not known. It is seen, however, that the high value for the C−C bond constant is consistent with the observed C−C distance in indicating some double bond character. Similar situation obtains in dimethyl acetylene, as shown in (189).

2) $B(OH)_3$ (boric acid)

By analogy with the other boron compounds discussed in § 2, C), one would expect the three B−O valence bonds to lie in one plane. Hence in considering those vibrations of the $B(OH)_3$ molecule which do not appreciably involve the H atoms, one may regard the molecule as a plane YX_3 structure having the symmetry D_{3h}. The Raman spectrum of boric acid in solution has recently been studied by Mitra[1] who found two weak lines at 515 and 986 cm^{-1} and an intense line at 872 cm^{-1}. This observation is consistent with the D_{3h} model (86). With the frequency 872 cm^{-1} for the totally symmetrical vibration ν_1, the constants $k-2k'$ in the potential (92) turn out to be 7.60×10^{5}. The two other frequencies 515 and 986 lead, however, to no real solutions for the constants $k-k'$ and k_{α}.

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[5] L. Pauling, H. D. Springall & K. J. Palmer, Jour. Am. Chem. Soc. 61, 927, (1939).

[6] G. Glockler & F. T. Wall, Jour. Chem. Phys. 5, 813, (1937).

[1] S. M. Mitra, Ind. Jour. Phys. XII, Pt. 1, 9, (1938); also L. Kahovec, Zeits. f. phys. Chem. B 40, 135, (1938), on other boric acid derivatives.

On including the H atoms in our consideration. the symmetry of the molecule probably becomes that of C_{3v}. Mitra observed in solid $B(OH)_3$ two intense lines at 3195 and 3290 cm^{-1}. Since other expected lines are not observed probably because of their low intensities, it is not possible to have a complete assignment of all the fundamental frequencies.

D) Molecules with Symmetry C_{2v}

1) $O(CH_2)_2$ (ethylene oxide), 2) $S(CH_2)_2$

According to the theory of directed valence, the structure of the ethylene oxide molecule should be one in which the O and the C atoms form an isoceles triangle and the planes of the CH_2 groups are perpendicular to the plane σ of the OC_2 ring. Another plane of symmetry v is perpendicular to σ and the C—C bond. The nature of the 15 normal vibrations, their symmetry properties and their selection rules are shown in Table LXXIX.

Vibrations		Symmetry			Selection rules	
Notation	Nature	class	σ	v	Infrared	Raman
v_1	v_1 in CH_2	A_1	s	s	$\mathfrak{M}_z$	p
v_2	v_2 in CH_2	A_1	s	s	,,	p
v_3	bending[1] of CH_2	A_1	s	s	,,	p
v_4	v_1 in OC_2	A_1	s	s	,,	p
v_5	v_2 in OC_2	A_1	s	s	,,	p
v_6	v_1 in CH_2	B_1	s	a	$\mathfrak{M}_x$	d
v_7	v_2 in CH_2	B_1	s	a	,,	d
v_8	bending of CH_2	B_1	s	a	,,	d
v_9	v_3 in OC_2	B_1	s	a	,,	d
v_{10}	v_3 in CH_2	B_2	a	s	$\mathfrak{M}_y$	d
v_{11}	rocking[1] of CH_2	B_2	a	s	,,	d
v_{12}	twisting[1] in CH_2	B_2	a	s	,,	d
v_{13}	v_3 in CH_2	A_2	a	a	ina.	d
v_{14}	rocking of CH_2	A_2	a	a	ina.	d
v_{15}	twisting in CH_2	A_2	a	a	ina.	d

Table LXXIX. Normal vibrations of ethylene oxide molecule.
The Z-axis is the intersection of σ and v; the X-axis in σ; the Y-axis in v.

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[1] By "bending" of CH_2 is meant the motion of the H atoms ⊥ to the plane of CH_2; rocking describes the motion of the CH_2 in the plane of the CH_2 group; twisting respresents torsional motion of the CH_2 about the bisector of the H—C—H bond angle. These descriptive notations are due to J. W. Linnett, Jour. Chem. Phys. 6, 692, (1938).

The Raman and the infrared spectra of ethylene oxide have been stludied by a number of authors[2], and more recently by Linnett[8]. The assignments of the observed frequencies given by the last author are shown in Table LXXX.

Assignment	Observed frequencies Raman	 Infrared
ν_1	3008 p	3030 *s*
ν_2	1492 p	1497 *m*
ν_3	1122 p	overlapped by 1168
ν_4	1270 p	1271 *s*
ν_5	807 d	811 *w*
ν_6	3008	ca. 3000
ν_7	?	1453 *w*
ν_8	1159 d	1168 *s*
ν_9	867 d	867 *s*
ν_{10}	3060 d	ca. 3000
ν_{11}	?	overlapped by 1168
ν_{12}	?	673 *w*
ν_{13}	3080 d	–
ν_{14}	?	–
ν_{15}	807	–
$2\nu_5$		1616 *w*
$\nu_5+\nu_9$		1650 *m*
$2\nu_9$		1721 *w*
$\nu_{11}+\nu_{12}$		1845 *vw*
$\nu_4+\nu_{12}$		1945 *w*
$\nu_8+\nu_9$		2020 *m*
$\nu_4+\nu_9$		2119 *w*
$\nu_3+\nu_8$		2278 *m*
$\nu_2+\nu_8$		2639 *w*
$\nu_2+\nu_4$		2786 *w*
$2\nu_7$	2917 p	
ν_1, $2\nu_2$	2960–3008 p	
$\nu_1+\nu_9$, $\nu_6+\nu_9$		3876 *w*
$\nu_1+\nu_4$		4292 *w*
$\nu_2+\nu_{10}$		4587 *w*
$2\nu_1$, $\nu_1+\nu_6$ etc.		6173 *w*

Table LXXX. Vibrational spectra of ethylene oxide.

It is seen from the above table that except for ν_{14} and ν_{11} which is overlapped by the intense band at 1168 cm^{-1}, our knowledge concerning the normal vibrations of the ethylene oxide molecule is fairly complete. Perhaps it would be desirable to examine the absorption bands, especially the overlapping ones, under higher dispersion and resolution.

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[2] Raman spectrum: Lespieau & Bourguel, Bull. Soc. Chim. 47, 1365, (1930); Timm & Mecke, Zeits. f. Physik 97, 221, (1935); polarization data from Ananthakrishnan, Proc. Ind. Acad. 4, 82, (1936); Infrared spectrum: L. G. Bonner, Jour. Chem. Phys. 5, 704, (1937).

[8] J. W. Linnett, *loc. cit.*.

Recently, Eyster[4] has observed some 14 bands of ethylene oxide and 7 bands of ethylene sulphide $S(CH_2)_2$ in the photographic infrared region. From the envelopes of some of the stronger bands and from the following approximate values for the principle moments of inertia calculated on the basis of reasonable molecular dimension (electron diffraction data of H. A. Lévy, quoted by Eyster),

$$\begin{aligned} O(CH_2)_2: \quad & I_A=I_X=31.8, \quad I_B=I_Z=39.2, \quad I_C=I_Y= \ \ 59.0\times 10^{-40} \\ S(CH_2)_2: \quad & I_A=I_Z=38.8, \quad I_B=I_X=74.8, \quad I_C=I_Y=102.0\times 10^{-40} \end{aligned} \tag{177}$$

it is possible to make the following assignments.

$O(CH_2)_2$ Obs. ν & band type	Assignment	$S(CH_2)_2$ Obs. ν & band type
8333		
8466		
8602.1 *A* or *C*		
8667.0 *B*	$3\nu_1$	8637 *A*
8767.3 *C*	$2\nu_1+\nu_{10}$	
8773.8 *A*	$3\nu_6$	8771.9 *B*
8815.8 *B*	$\nu_1+2\nu_6$	
8835.8 *C*	$2\nu_6+\nu_{10}$	8833.8 *C*
8881.3		8909
		8982
9021.7 *C*	$3\nu_{10}$	9080.2 *C*
9483		
9704		
9807		
11333 complex		11413 complex

Table LXXXI. Photographic bands of ethylene oxide and sulphide.

§6. Eight-atomic Molecules

A) Ethane Type Molecules

A molecule of the type possesses 18 vibrational degrees of freedom. There are 5 single vibrations, 6 doubly degenerate vibrations and a torsional oscillation (or retarded rotation) of the two CH_3 groups about the C—C axis. Of the 5 single vibrations, 2 are the in-phase and out-of-phase valence vibrations ν_1 in the CH_3 groups, 2 are the in-phase and out-of-phase deformation vibrations ν_3 in the two CH_3 groups (see Fig. 26), and one is the symmetrical vibration of the two CH_3 groups. Of the 6 degenerate vibrations, 2 are the valence vibrations ν_2 and 2 are the deformation vibrations ν_4 in the two CH_3 groups, and 2 are the bending motions of the CH_3 groups. The symmetry properties of these vibrations depend on the symmetry of the molecule, *viz.*, according as whether the molecule has a plane of symmetry perpendicular to the C—C axis (class D_{3h}), or a center of symmetry (class D_{3d}) so that the two CH_3 groups have their symmetry planes displaced by $\pi/3$, or the symmetry D_{3h}' in which the possibility of free rotation of the two groups about the C—C axis is taken into account in D_{3h}. The selection rules for the three cases are given in Table LXXXII.

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[4] E. H. Eyster, Jour. Chem. Phys. 6, 576, (1938).

Vibrations	D_{3h}'			D_{3h}			D_{3d}		
	Symm.	Inf.	Ram.	Symm.	Inf.	Ram.	Symm.	Inf.	Ram.
ν_1 ν_2 ν_3	A_1	—	p	A_1'	—	p	A_{1g}	—	p
ν_4 ν_5	$\bar{A}_2$	$\mathfrak{M}z$	—	A_2''	$\mathfrak{M}z$	—	A_{2u}	$\mathfrak{M}z$	—
ν_{12} torsion	$\bar{A}_1$	—	—	A_1''	—	—	A_{1u}	—	—
ν_6 ν_7 ν_8	E	$\mathfrak{M}x,y$	d	E'	$\mathfrak{M}x,y$	d	E_u	$\mathfrak{M}x,y$	—
ν_9 ν_{10} ν_{11}	$\bar{E}$	—	d	E''	—	d	E_g	—	d

Table LXXXII. Selection rules for D'_{3h}, D_{3h} & D_{3d} type Y_2X_6 molecules.

The selection rules for the harmonic and combination bands can be obtained on the following considerations of the symmetry properties:

$$A_1^n = A_1 \quad , \qquad A_2^n = \begin{cases} A_1 \text{ for } n \text{ even} \\ A_2 \text{ for } n \text{ odd} \end{cases}$$

$$A_1 \cdot A_2 = A_2 \quad , \qquad E^n = \begin{cases} A_1 + E \text{ for } n \text{ even} \\ A_1 + A_2 + E \text{ for } n \text{ odd} \end{cases} ,$$

$$A_1 \cdot E = A_2 \cdot E = E, \quad E \cdot E = A_1 + A_2 + E \, .$$

For the D_{3h} model,

$$(')^{n_1} \; ('')^{n_2} = \begin{cases} (') \text{ for } n_2 \text{ even} \\ ('') \text{ for } n_2 \text{ odd,} \end{cases}$$

and for the D_{3d} model,

$$(g)^{n_1}\ (u)^{n_2} = \begin{cases} (g) \text{ for } n_2 \text{ even} \\ (u) \text{ for } n_2 \text{ odd}. \end{cases}$$

From these and the selection rules in Table LXXXII, one can obtain the selection rules for any harmonic and combination bands in the Raman and the infrared spectra. An important difference between the D_{3h} and the D_{3d} models is that all harmonics of the E' fundamentals are active in absorption, while only the even harmonics (n odd) of the E_u fundamentals are allowed in absorption.

For the 5 single vibrations, the following modified valence force potential can be employed.

$$V = 6k(\delta r)^2 + k_1(\delta r_1)^2 + 6k_\theta(r\delta\theta)^2 + 6k_\varphi(s\delta\varphi)^2 + 12k_2(s\delta\varphi)\delta r_1, \qquad (178)$$

where r=C−H, r_1=C−C, $\theta=\widehat{HCH}$, $\varphi=\widehat{HCC}$. The equations for the symmetrical vibrations ν_1, ν_2, ν_3 are

$$\lambda_1+\lambda_1+\lambda_3=\left(\frac{1}{m}+\frac{3}{M}\cos^2\varphi\right)k+\left(\frac{1}{m}+\frac{3}{M}\sin^2\varphi\right)k_\alpha+\frac{2}{M}(k_1-6\sin\varphi\, k_2),$$

$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1=\frac{2}{mM}(k+k_\alpha)k_1+\frac{M+3m}{m^2M}kk_\alpha-\frac{12}{mM}\left[\sin\varphi\, k+k_2\right]k_2,$$

$$\lambda_1\lambda_2\lambda_3=\frac{2}{m^2M}(k_1k_\alpha-6k_2^2)k, \qquad (179)$$

where

$$k_\alpha = k_\varphi + k_\theta(r/s)^2\frac{12\cos^2\varphi}{1+3\cos^2\varphi}.$$

The equations for the vibrations ν_4 and ν_5 can be obtained from (179) by setting $k_1=k_2=0$. For the doubly degenerate vibrations, the equations are more complicated and will not be given here.

Another potential of the type (155) has been given by Sutherland and Dennison[1].

1) C_2H_6

The study of the spectrum of the ethane molecule is of special interest on account of the question concerning the potential energy of the molecule as a function of the relative orientation of the two CH_3 groups about the C–C axis. Whether the two CH_3 groups are more or less free to rotate relative to each other, or the motion is one of torsional oscillation about a position of equilibrium, and if so, whether the equilibrium configuration has the symmetry D_{3h} or D_{3d}, are questions of considerable importance since a knowledge of them will throw some light on the nature of the interactions between the H atoms in the two CH_3 groups in the ethane and other similar molecules.

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[1] G. Sutherland & D. M. Dennison, Proc. Roy. Soc. A 148, 250, (1935). Equations (179) with $k_2=0$ have been given by J. B. Howard, Jour. Chem. Phys. 5, 442, 451, (1937).

The infrared spectrum of C_2H_6 in the gaseous state was investigated under high dispersion by Levin and Meyer[2] and was later examined under lower dispersion but over a greater spectral range by a number of workers.[2] The Raman spectra of gaseous and liquid C_2H_6 have also been studied by a number of authors[3]. The following tables summarize the observed data and their interpretations.

Assignment		C_2H_6 gas		C_2H_6 liquid			
C. A. L.	B.	L. H.	Bh.	D.	G. R.	G. K.	C. A. L
$2\nu_{12}$					617 *vw*		620 *vw*
ν_6					813 *vw*	786(2)	820 *vw*
$\nu_1(C^{12}-C^{13})$			975		979 *w*	964(1)	
ν_1		993(3)	993(5)	990(3)	994	991(8)	993 p
		1344 ?				1335(2)	
ν_{10}	ν_7		1460 w	1460(1)	1463 *w*	1461(7)	1460 d
	ν_2					1491(3)	1480 p ?
$2\nu_2$	$2\nu_4$	2744(2)			2733	2729(6)	
$2\nu_4$	$2\nu_{10}$	2778(0)			2768	2791(4)	
ν_3	ν_3	2899(6)	2900(9)	2890(5)	2884	2876(10)	2900 p
$2\nu_{10}$		2955(7)	2955(10)	2950(5)	2941	2939(10)	2955 p
$2\nu_7, \nu_7+\nu_{10}$	$2\nu_2$	2940(1)			2922 *w*		
ν_{11}	ν_{11}				2963	2956(5)	

Table LXXXIII. Raman spectrum of C_2H_6
C. A. L=Crawford, Avery & Linnett; B.=Barker; L. H.=Lewis & Houston; Bh.=Bhagavantam; D.=Daure; G. R.=Glockler & Renfrew; G. K.=Goubeau & Karweil.

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[2] A. Levin & C. F. Meyer, Jour. Opt. Soc. Am. 16, 137, (1928); E.Bartholome & H. Sachsse, Zeits. f. phys. Chem. B 30, 40, (1935); E. Bartholome & J. Karweil, *ibid.*, B 39, 1, (1938); J. Karweil & K. Schäfer, *ibid.*, B 40, 382, (1938); B. L. Crawford, W. H. Avery & J. W. Linnett, Jour. Chem. Phys. 6, 682, (1938).

[3] P. Daure, Ann. de Phys. 12, 375, (1929); S. Bhagavantam, Ind. Jour. Phys. 6, 596, (1931); C. M. Lewis & W. V. Houston, Phys. Rev. 44, 903, (1933); G. Glockler & M. M. Renfrew, Jour. Chem. Phys. 6, 295, 409, (1938); Crawford, Avery & Linnett, *loc. cit.*; G. Goubeau & J. Karweil, Zeits. f. phys. Chem. B 40, 376, (1938).

Assignment C. A. L.	Assignment Ba	L. M.	B. S.	B. K.	C. A. L.
ν_6		827 *s* $\perp$			
ν_4		1379 *w* $\parallel$	1365		1380 *w*
$\nu_9+\nu_{12}$		1414 *w* $\perp$			1414 *w*
ν_7		1465 *s* $\perp$	1465 *s*		1477 *s*
			1495		
$\nu_{10}+\nu_{12}$					1740 *w*
$2\nu_9$				2230 *w* $\perp$?	
$\nu_6+\nu_7$				2303 *w* $\parallel$?	
$\nu_1+\nu_4$					2353 *w*
$\nu_{11}-\nu_{12}$				2674 *w* $\perp$	2660 *w*
$\nu_2+\nu_2$	$\nu_4+\nu_9+\nu_{12}$			2755 *m* $\parallel$	2755 *m*
ν_8		2895 *s* $\parallel$		2895 *m* $\parallel$	2895 *m*
$\nu_7+\nu_{10}$		2955 *s* $\parallel$		2954 *s* $\parallel$	2955 *s*
$\nu_1+\nu_6+\nu_9$		3015 *w*CH_4		3007 *m* $\parallel$	3007 *m*
ν_8		2990 *w* $\perp$		2950–3000 *w* $\perp$	2950-3000 *w*
$2\nu_6+\nu_7$				3100–3150 *w* $\perp$	3100-3150 *w*
$2\nu_{10}+\nu_{12}$				3186 *w* $\parallel$	3186 *w*
$\nu_7+\nu_9+2\nu_{12}$				3222 *w* $\parallel$	3222 *w*
				2195-3285 *w* $\perp$?	

Table LXXXIV. Infrared spectrum of C_2H_6
L. M.=Levin & Meyer; B. S.=Bartholomé & Sachsse; B. K.=Bartholomé & Karweil; C. A. L.=Crawford, Avery & Linnett; Ba=Barker.

The assignments of the fundamental frequencies can be made on the following considerations: From polarization measurements, it was found that the 993, 2900, 2955 cm^{-1} lines are polarized and the 1460 line depolarized. The 993 cm^{-1} must be one of the A_1 fundamentals. The presence of two Raman lines at 2900 and 2955 cm^{-1} can be explained as due to a resonance between the A_1 fundamental in this region and the harmonic of an E fundamental at *ca.* 1450 cm^{-1}. The other A_1 fundamental due to the deformation vibration in CH_2 is expected to lie at *ca.* 1400 cm^{-1}. Crawford, Avery and Linnett suggested that it is not observed but its harmonic and the harmonic of the A_2 fundamental ($\nu_4 \sim$ 1379) are responsible for the resonating pair of weak Raman lines at 2774 and 2778 cm^{-1}. (It has recently been pointed out by Barker[4] that the 1460 cm^{-1} line shows a weaker satellite at *ca.* 1480 cm^{-1} which seems to be polarized and that this is probably the A_1 fundamental in this region). The intense parallel type bands at 1379 and 2955 cm^{-1} can be assigned to the A_2 fundamentals. The presence of three parallel bands at 2895, 2955 and 3007 cm^{-1} can again be explained as the result of resonance interaction among three levels as shown in Table LXXXIV. The perpendicular type bands at 827, 1460 and 2980 cm^{-1} can be ascribed to the E' or E_u fundamentals. The E'' or E_g fundamental in the region 3000 cm^{-1} may be identified with the weak Raman line 2960 cm^{-1}. The

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[4] E. F. Barker, Jour. Chem. Phys. 7, 277, (1939).

E'' or E_g fundamental in the region 1400 cm^{-1} should be Raman effect active, and is probably the 1460 Raman line. (According to Barker, this is not observed, but the pair at 2744 and 2778 cm^{-1} may be due to the resonance between $2\nu_4$ and the harmonic of this E'' or E_g fundamental). This now leaves only the torsional vibration (or retarded rotation) and one of the E'' or E_g fundamentals undetermined.

As already mentioned, the question concerning the nature of the torsional degree of freedom is of great interest. Since this degree of freedom is inactive in both the absorption and the Raman spectra for both the D_{3h} and the D_{3d} models, information concerning it can be obtained only through its possible occurrence of its first harmonic in the Raman spectrum, or through its contribution to the specific heat of the molecule. Theoretically, this contribution can be calculated from the state sum (Zustandssumme)[5]

$$Q = \Sigma g_i e^{-\frac{E_i}{kT}} \tag{180}$$

by means of the equation (143) in Chap. III,

$$C_v = R\sigma^2 \frac{d^2 \ln Q}{d\sigma^2} \tag{181}$$

where $\sigma = 1/kT$ and E_i are the energy levels for this degree of freedom of motion, and are the eigenvalues of the Schrödinger equation (120) of Chap. III. As a first approximation, one may assume the simple from

$$V(\varphi) = A \cos 3\varphi \tag{182}$$

for the potential energy of the two CH_3 groups, and for this the Schrödinger equation is the well known Mathieu equation. Teller and Weigert[5] took into account in their calculation three spin modifications of the C_2H_6 molecule, while more recently Schäfer[5] and also Wilson carried out a similar calculation with all nine spin modifications (of which only six are independent) taken into account. These authors showed that at temperatures (above 100°K) for which specific heat data are available, the effect of the statistical weights due to the nuclear spins of the H atoms is negligible. For this reason, the simpler calculations of Pitzer and Kemp which neglect the nuclear spins are justified.

Experimentally, the specific heat of ethane has been the subject of measurements by Eucken and his coworkers in the Göttingen laboratory and by Kistiakowsky and his coworkers in the Harvard laboratory.[6] Their results are shown in Fig. 37.

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[5] E. Teller & K. Weigert, Gött. Nachr. 218, (1933); J. D. Kemp & K. S. Pitzer, Jour. Am. Chem. Soc. 59, 276, (1937); K. S. Pitzer, Jour. Chem. Phys. 5, 469, (1937); W. Hunsmann, Zeits. f. phys. Chem. B 39, 23, (1938); K. Schäfer, *ibid.*, B 40, 357, (1938); E. B. Wilson, Jr., Jour. Chem. Phys. 6, 408, 740, (1938).

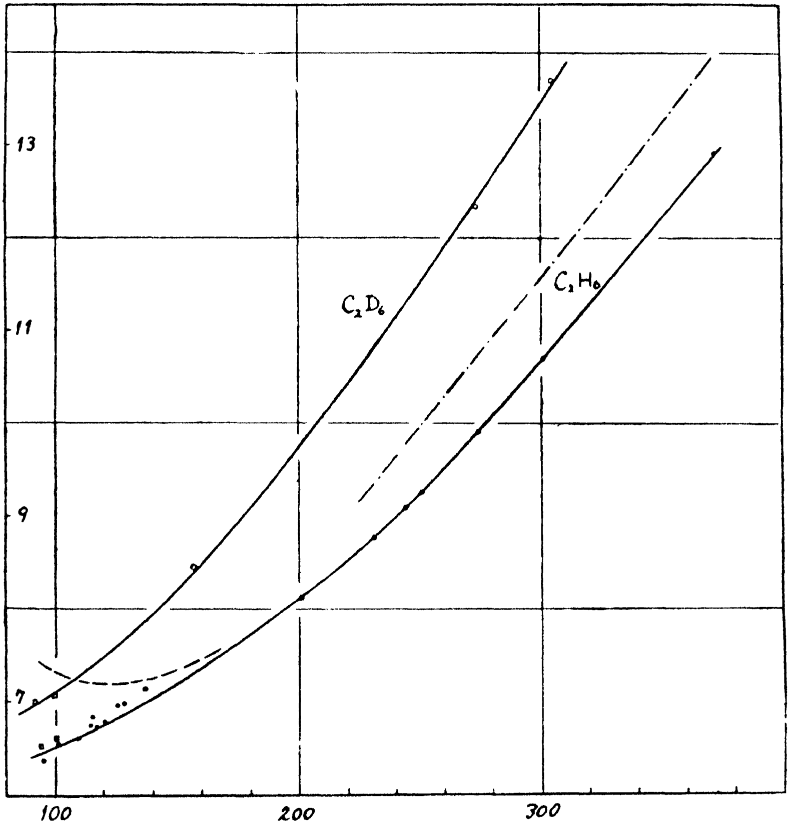

Fig. 37. Theoretical and observed vibrational specific heats of C_2H_6 and C_2D_6. Ordinates are in calories per mole; abscissa are temperature in degrees K.
Experimental points: dots are from the Eucken laboratory; squares from the Harvard laboratory. Theoretical curves: Solid curves are calculated with the frequencies in Table LXXXV and a barrier 2A$\sim$ 3000 cal/mole; Curve in dashes is obtained with $\nu_9 \simeq$ 740 cm^{-1} and 2A $\simeq$ 310 cal/mole; Curve in dashes and dots is obtained with $\nu_9 \simeq$ 740 cm^{-1} and 2A $\simeq$3000 cal/mole.

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[6] A. Eucken & A. Parts, Zeits. f. phys. Chem. B 20, 184, (1933), down to 190°*K*; Eucken & K. Weigert, *ibid.*, B 23, 265, (1933), down to 140°*K*; Eucken & Bertram, *ibid.*, 31, 363, (1936), down to 170°*K*; W. Hunsmann, *ibid.*, B 39, 23, (1938), down to 95°*K*; G. Kistiakowsky and F. Nazmi, Jour. Chem. Phys. 6, 18, (1938), down to 140°*K*; Kistiakowsky, J. R. Lacher & F. Stitt, *ibid.*, 7, 289, (1939), down to 94°*K* and also the specific heat of C_2D_6 at 94° and 100°*K*.

From the observed specific heats and the calculated values, it would seem easy indeed to decide between a torsional oscillation (high potential barrier) and a free or retarded rotation (low potential barrier). This however is not the case, as one of the E'' or E_g fundamentals is not known. On the basis of the calculations of Teller and Weigert, Eucken and Parts concluded from their specific heat data down to 190°K that the best fit between the observed and the calculated specific heats is obtained by assuming the frequency E'' or E_g to be *ca.* 740 cm^{-1} and a retarded rotation corresponding to a value $2A=315$ calories per mole (*ca.* 110 cm^{-1}). Bartholomé and Karweil showed later that all the observed bands can be satisfactorily accounted for on the assumption of E'' or $E_g \sim 740$ cm^{-1}. The measurements of the specific heat at lower temperatures (down to 100°K) by Hunsmann and by Kistiakowsky and his coworkers showed, however, that the observed data can only be accounted for by the assumption of a value *ca.* 1120 cm^{-1} for the E'' or E_g fundamental and a torsional oscillation corresponding to a value $2A=3400$ calories/mole, as shown in Fig. 37. It has been shown by Crawford, Avery and Linnett that a satisfactory assignment can be given to all the observed bands on this assumption, as shown in Tables LXXXIII and LXXXIV. Hence it appears that the present specific heat and the vibbrational spectrum data are in agreement with a high potential barrier of *ca.* 3000 calories/mole between the D_{3h} and the D_{3d} configurations.[7]

On accepting the value $\simeq$ 3000 calories/mole for the potential barrier, the next quėstion is whether the D_{3h} or the D_{3d} configuration has the minimum potential energy. With the well known potential curve for two hydrogen atoms (whose electrons are already paired) and taking into account the Van der Waals attractions between the hydrogen atoms in the two CH_3 groups, Eyring[8] has calculated the potential $V(\varphi)$ and found $2A \sim 350$ cal/mole, with the minimum at the D_{3d} configuration. This theoretical value is far too low compared with the value$\sim$3000 cal/mole obtained from the thermal data. The cause of this great discrepancy is not known.[8] From the spectroscopic data now available, it is not yet possible to draw a definite conclusion as to whether the D_{3h} or the D_{3d} configuration is the one of stable equilibrium, although it seems that the D_{3h} seems slightly more satisfactory.[9]

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[7] Besides the spectroscopic and the specific heat data, the value of the entropy of the ethane gas at 25°C and one atmosphere pressure obtained by R. K. Witt & J. D. Kemp, Jour. Am. Chem. Soc. 59, 273, (1937), namely, 54.85 calories per mole per degree, is also in agreement with the value 54.70 obtained theoretically by Schäfer, footnote (5), with $\nu_9(E'') \simeq 1130$ cm^{-1} and $2A \simeq 3000$ cal/mole. Very recently, from the specific heat data of C_2H_6 and C_2D_6 down to 93°K, Kistiakowsky, Lacher, & Stitt, footnote (6), arrives at the values $\nu_9(E'')=1170$ cm^{-1} and $2A=2750$ cal/mole. The calculated entropy $S^{298}=$for C_2H_6 is then 54.95. This potential leads to the following energy levels for the torsional oscillation in C_2H_6: $v_{12}=1$, 275 cm^{-1}; $v_{12}=2$, 520 cm^{-1}; in C_2D_6: $v_{12}=1$, 200 cm^{-1}; $v_{12}=2$, 380 cm^{-1} (each of these levels really consists of four slightly distinct levels, two of which are doubly degenerate, as shown in Fig. 15b). While these levels are in very good agreement with the specific heat data, the value 520 cm^{-1} leaves the weak Raman line at 620 cm^{-1} unexplained (the 620 line may be ascribed to $2\nu_{12}$ if the potential barrier is nearer 3400 cal/mole than 2750 cal/mole).

Let us now consider the potential of the C_2H_6 molecule. With the potential (178) and the two infrared parallel frequencies $\nu_4=1380$, $\nu_5=2926$ which are quite definite, one obtains

$$k_{CH} = 4.87\,, \qquad k_{\alpha} = 0.92\,. \tag{183a}$$

With these values and the assignments $\nu_1=993$, $\nu_2=1375$, $\nu_3=2927$ of Crawford, Avery & Linnett, equations (179) lead to no solutions for the constants k_{CC} and k_2. They can be satisfied, however, approximately by the values

$$k_{CC} = 4.50\,, \qquad k_2 = 0.19\,. \tag{183b}$$

Recently, Stitt[10] has employed a potential that contains in addition to the terms in (178) also cross terms in the various angles ϑ and φ. With such a potential, the eleven frequencies ν_1 to ν_{11} in both C_2H_6 and C_2D_6 can be reproduced fairly well. We shall give these calculated frequencies in Table LXXXV below.

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[8] H. Eyring, Jour. Am. Chem. Soc. 54, 3191, (1932). Eucken and K. Schäfer, Naturwiss. 27, 127, (1939), showed recently by a pure electrostatic consideration and a qualitative wave mechanical calculation that the energy difference between D_{3d} and D_{3h} is $\sim$ 3000 cal/mole, with the latter more stable. See (9) below.

[9] It has been shown by Crawford, Avery & Linnett, footnote (2), that a satisfactory assignment of the infrared and Raman frequencies can be given on either the D_{3h} or the D_{3d} model, but the numerical agreement between the calculated and the observed frequencies is slightly better in the case of the D_{3h} model. The weak Raman line at 820 cm^{-1}, if it is really due to C_2H_6, can only be explained as ν_6 and according to the selection rules in Table LXXXII, the symmetry must be D_{3h}. If one accepts Barker's assignment in Tables LXXXIII and LXXXIV, then the symmetry must be D_{3h} because of the appearance of ν_7 in the Raman spectrum. On the other hand, the interpretation of the heats of hydrogenation of a number of unsaturated cyclic hydrocarbons favors the D_{3d} as the more stable configuration, as given in a preliminary remark by Kistiakowsky, Lacher and Stitt, Jour. Chem. Phys. 7, 289, (1939).

1a) C_2D_6 (hexadeutero-ethane)

Recently, Stitt[1] has studied the absorption (under low dispersion) and the Raman spectrum (polarization measurements) of C_2D_6. The observed data and their interpretations are summarized in Table LXXXV, together with the corresponding frequencies in C_2H_6 and the calculated frequencies obtained by Stitt with a potential function containing 9 constants (for the D_{3d} model).

Assignment		C_2D_6 Obs. ν	C_2D_6 Calc. ν	C_2H_6 Obs. ν	C_2H_6 Calc. ν
A_{1g}	ν_1	852 s p	845	993	1010
	ν_2	1158 m p	1140	(1375)	1375
	ν_3 }	{2083 s p	2100	2925	2900
	$2\nu_{10}$ }	{2147 s p			
A_{2u}	ν_4	1072 s Inf.	1060	1380	1390
	ν_5	2100 s Inf.	2085	2925	2895
E_u	ν_6	601 s Inf.	600	827	830
	ν_7	1102 s Inf.	1080	1465	1495
	ν_8	2237 s Inf.	2240	2980	3020
E_g	ν_9	~ 970 w d	930	(1170)	1200
	ν_{10}	1055 m d	1055	1460	1445
	ν_{11}	2225 s d	2260	2960	3020
Torsion	ν_{12}	(200)		(275)	
	$\nu_6+\nu_{10}$	1654 w Inf.			
	$\nu_1+\nu_4$	1908 w Inf.			
	$2\nu_9$	~1930 vw Ra.			
	$2\nu_2$	~2300 w p			
	$\nu_{11}+\nu_{12}$	2415 w Inf.			
	$\nu_8+\nu_6$	2711 w Inf.			

Table LXXXV. Vibrational spectra of C_2D_6 and C_2H_6

The torsional frequency 200 cm^{-1} in C_2D_6 is obtained with the potential (182) and the value $2A=2750$ calories/mole. The specific heat of C_2D_6 has been recently measured by Kistiakowsky and his coworkers down to the temperature of 93°K.[2] The calculated specific heat obtained with the frequencies in LXXXV is in very good agreement with the observed values. Another check for the correctness of the assignments of the fundamental frequencies in C_2D_6 and C_2H_6 is furnished by the socalled "product rules" which are relations connecting the products of the frequencies of vibrations belonging to the same symmetry class and

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[10] F. Stitt, Jour. Chem. Phys. 7, 297, (1939).

[1] F. Stitt, Jour. Chem. Phys. 7, 297, (1939).

[2] G. B. Kistiakowsky, J. R. Lacher & F. Stitt, *ibid.*, 7, 289, (1939).

of the frequencies of the corresponding vibrations in an isotopic molecule (the last equation in (179), for example). It is found that when due account is taken of the anharmonicity corrections, the frequencies given in Table LXXXV satisfy these "product relations" very well.

Just as in the case of C_2H_6, it is as yet not possible to decide on the symmetry (D_{3h} or D_{3d}) of the molecule from the vibrational spectrum, since the few Raman lines and infrared bands can be equally well accounted for in accordance with the selection rules for both models.

2) Si_2H_6, 3) C_2Cl_6, 4) Si_2Cl_6, 5) B_2H_6

These molecules are presumably of the ethane type. Their Raman spectra have been studied by various authors[1], but the data are too meagre for a complete determination of the normal frequencies of the molecules. Table LXXXVI summarizes the observed data and their tentative interpretations. Until more data are available, we shall refrain from any calculation of the force constants of these molecules.[2]

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[1] Si_2H_6 and Si_2Cl_6, F. Stitt & D. M. Yost, Jour. Chem. Phys. 5, 90, (1937); C_2Cl_6 polarization data from F. Heidenreich, Zeits. f. Physik 97, 277, (1935); B_2H_6, T. F. Anderson & A. B. Burg, Jour. Chem. Phys. 6, 568, (1938). The 980 cm^{-1} of C_2Cl_6 was observed only by Ananthakrishnan, Proc. Ind. Acad. Sci. A 5, 285, (1937).

[2] From the three totally symmetrical vibrations in C_2H_6, Si_2H_6, B_2H_6, Anderson and Burg, *loc. cit.*, have calculated the constants in a simple valence force potential ($k_2=0$ in 178). The values for the C—C, Si—Si, B—B bond constants are 5.6, 1.7, 3.57×10^5 respectively. The bond distances calculated from the Badger relations with these constants are 1.35, 2.13, 1.48 Å compared with the electron diffraction values 1.55, 2.32, 1.86 Å respectively. The differences they attribute to a state of compression of the two central atoms which may arise from the interactions between the H atoms in one YH_3 groups and the X—H bonding orbitals in the other YH_3 group. But this can hardly explain the differences between the calculated and the observed bond lengths, for if the central atoms are actually compressed, the effect would also manifest itself in the electron diffraction values. It is more probable that the force constants are too high. See Sec. 3, B, 4) CF_4, footnote (6), and the C—C constant in (183b).

Si_2H_6 (gas) Obs. ν		C_2Cl_6(liq) Obs. ν		Si_2Cl_6 (liq) Obs. ν		B_2H_6(liq) Obs. ν	
434.5 *m*	*A*(Si-Si)	142 *w* p	$A(\delta_\pi)$	124 (6) 0.72	$A(\delta_\pi)$	792.5(5)	$A(B^{11}\text{-}B^{11})$
910—		216 *m* d	$E(\delta'_\sigma)$	132	$E(\delta_\sigma)$	806.2(4)	$A(B^{11}\text{-}B^{10})$
—955 *w*	$E(\delta_\sigma)$	342 *m* d	$E(\delta_\sigma)$	212(4) d	$E(\delta_\sigma)$	821.4(3)	$A(B^{10}\text{-}B^{10})$
2163 *s*	$A(\nu_\pi)$	432 *s* p	$A(\nu_\pi)$	354(10) p	$A(\nu_\pi)$	1180.4(2)	$A(\delta_\pi)$
		860 *s* d	$E(\nu_\sigma)$	378	252+ 124	2102 (10)	$A(\nu_\pi)$
		980 *w* ?		387	132	2523 (10)	$2\delta_\pi$
				421 *vw*	$2\delta'_\sigma$	2489 (3)	
				460 *vw*	252+212	2775 (3)	
				487 *vw*	$\nu_\pi+\delta_\pi$	2868 (2)	
				590(3) d	$E(\nu_\sigma)$	3120 (2)	
				565 *vw*	$\nu_\pi+\delta_\sigma$		
				625(2) p	$2\nu_{\pi a}$		
				706 *vvw*	$2\nu_{\pi s}$		

Table LXXXVI. Raman spectra of Si_2H_6, C_2Cl_6, Si_2Cl_6, B_2H_6

B) Ethane Derivatives

1—5) 1,2 dihalogen derivatives of ethane

In view of the question concerning the internal rotation or torsional oscillation in the ethane molecule, the study of the spectra of the 1,2 dihalogen derivatives of ethane is also of considerable interest. The infrared spectra of $C_2H_4Cl_2$, C_2H_4ClBr, $C_2H_4Br_2$, C_2H_4ClI, $C_2H_4I_2$ in the region between 500 and 1400 cm^{-1} have been studied under low dispersion by Cheng and Lecomte[1]; the Raman spectra and polarization characters have been studied by Cheng and others.[2] Of special interest is the study by Mizushima and Morino[3] of the Raman spectra of $C_2H_4Cl_2$ and $C_2H_4Br_2$ in the solid state at $-40°C$. They found that a large number of lines in each molecule disappeared at this temperature while other lines remained undiminished in intensity. On regarding these molecules as 4-particle systems $X-(CH_2)-(CH_2)-X$, Cheng and Lecomte and the other authors concluded that both the *trans* and the *cis* forms of these molecules exist and that an assignment can be given of the infrared and Raman frequencies to the 6 fundamental vibrations in each isomer on considerations of the selection rules. It has been shown by Wu[4] that a satisfactory assignment can also be given to the 18 normal vibrations of each molecule regarded as an 8-particle system. Table LXXXVII gives the selection rules for both the *trans* and the *cis* isomers; Table LXXXVIII summarizes the observed data; and Tables LXXXIX and XC give the assignments.

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[1] H. C. Cheng & J. Lecomte, Jour. de Phys. et Rad. 6, 477, (1935).

[2] H. C. Cheng, Jour. de Chim. Phys. 32, 715, (1935); Kohlrausch & Ypsilanti, Zeits. f. phys. Chem. B 29, 274, (1935); B. Trumpy, Zeits. f. Physik 93, 624, (1935); Ananthakrishnan, Proc. Ind. Acad. Sci. A 5, 285, (1937)); J. Cabannes, Jour. de Chim. Phys. 35, 1, (1938).

[3] S. Mizushima & Y. Morino, Bull. Chem. Soc. Jap. 13, 182, (1938).

Symmetry C_{2h} (*trans*)						Symmetry C_{2v} (*cis*)					
class	σ	i	Vib's	Inf.	Ram.	class	σ	ν	Vib's	Inf.	Ram.
A	s	s	6	ina.	p	A_1	s	s	6	act.	p
B	s	a	5	act.	ina.	B_1	s	a	5	act.	d
B'	a	s	3	ina.	d	B_2	a	s	3	act.	d
A'	a	a	4	act.	ina.	A_2	a	a	4	ina.	d

Table LXXXVII. Selection rules of *trans* & *cis* XCH_2-CH_2X.

The assignments given in Tables LXXXIX and XC are guided by the following considerations of the nature of the various normal vibrations. In class A or A_1, one vibration is roughly a vibration in the C$-$C bond, one in the C$-$X bonds, two are the symmetrical valence and deformation vibrations ν_1 and ν_2 in the CH_2 groups, one is the deformation vibration of the (CH_2) groups with respect to the C$-$C axis, and one the deformation vibration of the (CH_2X) groups with respect to the C$-$C axis. In class B or B_1, the vibrations are essentially the same as the last 5 vibrations in class A or A_1, except that the vibrations in the two CH_2X groups are out of phase. In class B' or B_2, one vibration involves the valence vibration ν_3 in the CH_3 groups, one a turning of the CH_2 groups about the bisectors of the H$-$C$-$H angles, and one a motion of the C atoms perpendicular to the plane of X$-$C$-$C$-$X. In class A' or A_2, three of the vibrations are the out-of-phase vibrations of those in class B' or B_2, and the last is a torsional vibration of the two CH_2X groups.

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[4] T. Y. Wu, Jour. Chem. Phys. 7, Oct. (1939).

Cl-Cl		Cl–Br		Br–Br		Cl-I		I-I.	
Ram.	Inf.	Ram.	Inf.	Ram.	Inf.	Ram.	Inf.	Ram.	Inf.
123(4)d				92(2)d?					
263(2)p		246p(10)		230(1)p		229(8)			
*302(8)p		211p(1)		*189(10)p		183(4)			
411(3)d		386d(3)		359(2)d		365(2)			
654(10)p	656*s*	568p(9)	569*s*	551(8)p	550*s*	510(5)			
675(3)d	676*s*	630p(8)	631*s*	583(2)d	587*s*	574(10)	576*s*	512	
	707*s*	662d?(5)	664*w*			655(2)	655*s*		635*s*
*754.15)p		720p(14)	722*s*	*659(15)p		703(12)	702*s*	582	
	759*w*		756*w*		750*s*		740*w*		720*s*
880(1)d	878*m*	852 (½)	858*m*	834(½)d	834*s*	820(0)	817*m*		778*m*
940(2)p	940*m*	919p(2)	917*m*	897(1)p	896*m*	904(0)	896 *w*		840 *w*
*989(1)				*930(1)p					
1031(1)	1015*w*	1019 (0)	1020*w*	1019(½)?					
*1052(1)p		1050 (3)		*1052(6)d?		1040(3)	1030*w*		
	1092*ww*		1090 *ww*		1075*ww*				1040*w*
1144(½)d		1120(½)		1096 ?					
1206(2)d		1180(½)				1150(4)			
	1243*m*	1200(3)	1201*m*		1191*s*		1132*m*		1128*s*
*1262(½)d		1256(2)		*1169(½)d		1231(0)			
*1302(2)p		1280(4)		*1256(10)p		1270(4)			
1393(½)		1345(0)		1295(1)p					
1429(3)d	1400*m*	1425(3)	1400*m*	1419(1)d	1400*m*	1435(1)	1400*m*		1400*m*
*1440(½)d				*1436(2)d					
2844(1)?		2863(1)		2950(6)p					
*2872(1)p				*2852(1)p					
*2956(12)p	3000*s*	2962(10)		*2970(8)p	3000*s*	2952(0)			
*3002(4)d		3010(2)		*3012(2)d					
				132(2)?					
				320(½)?					
				470(½)?					
				790(0)?					

Table LXXXVIII. Vibrational spectra of 1,2 dihalogen ethanes. The frequencies marked with * are those which do not disappear in the Raman spectra of the crystals at −40°*C*.

In the actual assignments, those frequencies that do not disappear in the Raman spectra of the solids at −40°C are ascribed to the *trans* forms[5], while those appearing in both the absorption and the Raman spectra must according to the selection rules be ascribed to the *cis* forms.

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[5] That only the *trans* form is present in the solid at low temperatures is supported by the observation of A. H. White & S. O. Morgan, Jour. Chem. Phys. 5, 655, (1937), that there are sudden drops in the values of the dielectric constants of these substances at low temperatures.

A	ν_{C-C}		ν_{C-X}		$\nu_1(CH_2)$		δ in CH_2		$\delta(CH_2)$		$\delta(CH_2X)$	
	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.
Br-Br	930p	–	658p	–	2970p	–	1256p	–	1051d?	–	187p	–
Br-Cl			720p	722			1280		1050		211p	
Cl-Cl	990	–	750p	–	2956p	–	1302p	–	1052p	–	300p	–
Cl-I			703	702			1270		1040	1030		
I-I		–	582	-		–		–		–		–

B	ν_{C-X}		$\nu_1(CH_2)$		δ in CH_2		$\delta(CH_2)$		$\delta(CH_2X)$
Br-Br	–		–	3000	–	1400	–	1075	–
Br-Cl	662d	664		3000		1400		1090	
Cl-Cl	–	707	–	3000	–	1400	–	1092	–
Cl-I	655	655		3000		1400			
I-I	–	635	–	3000	–	1400	–	1040	–

B′	$\nu_8(CH_2)$		turning of CH_2		$\delta'(CH_2X)$	
Br-Br	3012d	–	1436d	–	1169d	–
Br-Cl						
Cl-Cl	3002d	–	1440d	–	1265d	–
Cl-I						
I-I		–		–		–

A′	$\nu_8(CH_2)$		turning of CH_2		$\delta'(CH_2X)$		torsion
Br-Br	–	3000	–	1191	–	750	–
Br-Cl		3000	1200	1201		756	
Cl-Cl	–	3000	–	1243	–	760	–
Cl-I		3000		1132		740	
I-I	–	3000	–	1128	–	720	–

Table LXXXIX. Fundamental frequencies of 1, 2 dihalogen ethanes (*trans*)

The presence of the weak and polarized lines 2872 cm^{-1} in *trans* $C_2H_4Cl_2$ and 2852 cm^{-1} in *trans* $C_2H_4Br_2$ can be explained as arising from a resonance between the *A* fundamental and the harmonic of the *B′* fundamental at *ca.* 1440 cm^{-1}. The depolarized lines 123 cm^{-1} in $C_2H_4Cl_2$ and 92 cm^{-1} in $C_2H_4Br_2$ which are not found in the solid at $-40°C$ must be ascribed to the torsional vibrations of the *cis* forms, as there is no other place for such a low frequency fundamental (see Table XC) and there is no simple way of assigning them to difference frequencies. Hence it may be concluded that the vibrational spectrum data establish the existence of both the *trans* and the *cis* forms in the liquid at ordinary temperatures.

A_1	$\nu_{C\text{-}X}$		$\nu_{C\text{-}X}$		$\nu_1(CH_2)$		δ in CH_2		$\delta(CH_2)$		$\delta(CH_2X)$	
	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.	Ra.	Inf.
Br-Br	897p	896	551p	550	2950p	3000	1295p		1019?	1000	230p	
Br-Cl	919p	917	568p	569		3000					246p	
Cl-Cl	940p	940	653p	653	2956p	3000	1393?	1400	1031?	1015	264p	
Cl-I	904	896	510			3000						
I-I		840				3000						

B_1	$\nu_{C\text{-}X}$		$\nu_1(CH_2)$		δ in CH_2		$\delta(CH_2)$	$\delta(CH_2X)$
Br-Br	583d	587	3012d	3000	1419d	1400	1086?	358d
Br-Cl	630p	631		3000		1400	1120?	386d
Cl-Cl	675d	675	3002d	3000	1429d	1400	1144d	411d
Cl-I	574	576		3000		1400		365
I-I	512			3000		1400		

B_2	$\nu_3(CH_2)$		turning of CH_2	$\delta'(CH_2X)$	
Br-Br	3012d	3000		834d	834
Br-Cl		3000		852	858
Cl-Cl	3002p	3000		880d	880
Cl-I		3000			817
I-I		3000			778

A_2	$\nu_3(CH_2)$		turning of CH_2	$\delta'(CH_2X)$		torsion	
Br-Br	3012d	–	–	1187?	–	92d	–
Br-Cl				1180?			
Cl-Cl	3002d	–	–	1206?	–	123d	–
Cl-I				1150			
I-I		–	–		–		–

Table XC. Fundamental frequencies of 1,2 dihalogen ethanes (*cis*)

The temperature variations of the electric moments of the $C_2H_4Cl_2$, C_2H_4ClBr, $C_2H_4Br_2$ have been studied by Zahn and by Williams.[6] From the observed increase of the electric moments with temperature, Altar and more recently Beach and Stevenson[7] have tried to determine the potential $V(\varphi)$, represented by a two-term Fourier series and a cosine function respectively, for the relative orientation φ of the two CH_2X

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[6] C. T. Zahn, Phys. Rev. 38, 521, (1931); 40, 291, (1932); E. W. Greene & J. W. Williams, *ibid.*, 42, 119, (1932).

[7] W. Altar, Jour. Chem. Phys. 3, 460, (1935); J. Y. Beach & D. P. Stevenson, *ibid.*, 6, 635, (1938).

groups. The assumption is made that the number of molecules with the two groups at an angle φ is proportional to the Boltzmann factor exp $(-V/kT)$. The potentials so obtained have their minimum at the trans position which is about 4-5 kcal/mole below the maximum at the *cis* position. On the same assumption concerning the distribution of molecules according to the Boltzmann factor, Beach, Palmer and Turkevich[8] have calculated the intensity patterns of the diffracted electrons with potentials $V(\varphi)$ obtained by combining the electrostatic repulsions between the halogen atoms and the exchange repulsions between the various atoms in the two CH_2X groups calculated by the method of Eyring[9] for the ethane molecule, and compared with the observed intensity patterns for $C_2H_4Cl_2$, C_2H_4ClBr and $C_2H_4Br_2$. They found that after a semi-empirical correction that raises the calculated potentials near the *cis* position by about 2 kcal/mole, the calculated intensity patterns approximate the observed ones very well. These resultant potentials place the *trans* positions in these molecules at about 6−7 kcal/mole below the maxima at the *cis* positions. With these potentials, however, the Boltzmann factor at room temperatures is so small that no Raman lines of the *cis* forms of these molecules should have been observable at all.

To understand this difference, it has been suggested by Wu[4] that the theoretical potentials of Beach *et al* may not be correct since the same method of calculating the exchange repulsions in the ethane molecule has led to the value 350 cal/mole for the potential barrier in complete disagreement with the value 3000 cal/mole established on specific heat, entropy and spectrum data (see last section on C_2H_6); that on accepting the empirical value 3000 cal/mole and the symmetry D_{3h}[10], it is not difficult to introduce a relative minimum in the potential at the *cis* position, which is still 5-6 kcal/mole above the minimum at the *trans* position and about 1 kcal/mole below the top of the potential barrier; and that such a potential can still be consistent with the temperature variations of the electric moments and the electron diffraction data. Such a potential, however, will explain the spectra of the *cis* isomers in Table XC, and in particular the torsional frequencies. The existence of a potential barrier between the *trans* and the *cis* positions requires, however, an activation energy for the transformation of one isomer to the other, and implies a dependence of the relative populations of the two configurations on the conditions under which the substance is treated. Further theoretical study of the interactions between the atoms in the two CH_2X groups and experimental work on the electric moments and the spectra of these molecules under different conditions will be necessary to settle this problem.

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[8] Beach & K. J. Palmer, *ibid.*, 6, 639, (1938); Beach & A. Turkevich, Jour. Am. Chem. Soc. 61, 303, (1939).

[9] H. Eyring, Jour. Am. Chem. Soc. 54, 3191, (1932).

[10] See footnote (8) in section on C_2H_6, however.

6) $C_2H_2Cl_4$, 6a) $C_2D_2Cl_4$, 7) $C_2H_2Br_4$

The Raman spectra of these molecules have been studied by a number of authors[1]. Because of the closeness of low frequency Raman lines, any assignments of the fundamental frequencies as given for the 1,2 dihalogen derivatives in Tables LXXXIX and XC will be uncertain, especially in the absence of infrared data. From the large number of Raman lines observed (9 polarized lines in $C_2H_2Cl_4$ and 14 in $C_2H_2Br_4$), it seems that more than one forms of the molecules are responsible for the observed spectra.

$C_2H_2Cl_4$	$C_2D_2Cl_4$	C_2H_2Br
90 w p	89(4b)	61(6b)d
171(5)p	176(4)	147(4) p
224(2)	225(½)	175(5) d
238(4)p	240(3)	184(1) d
289(4)0.7	292(4)	197(½)d
324(0)	316(0)	
353(8)p	351(7)	220(10)p
400(?)p	398(1)	242(1) p
514(2)d	533(2)	450(4) d
647(6)p	623(6)	537(8) p
760 w p	701(2)	665(4) p
799(7b)p	738(5)	713(15)0.68
		740(0) p
		800(0) d
1017(1)	829(1)	1012(3) p
		1030(1) p
1215(1)d	946(3)	1140(1) d
		1151(2) d
		1196(4) p
1242(0)		1222(½)p
1276(0)	1003(½)	1250(½)d
1306(0)	1098(½)	1281(1) p
		1405(½)p
2983(9)p	2339(5)	2985(4) p

Table XCI. Raman spectra of $C_2H_2Cl_4$, $C_2D_2Cl_4$, $C_2H_2Br_4$

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[1] B. Trumpy, Zeits. f. Physik 93, 624, (1935); 98, 624, (1936); H. Gockel, Zeits. f. phys. Chem. B 27, 79, (1935); Kohlrausch and Ypsilanti, *ibid.*, B 29, 274, (1935); R. Ananthakrishnan, Proc. Ind. Acad. Sci. A, V, 285, (1937).

§7. Nine-atomic Molecules

1) Cyclopropane C_3H_6

The infrared and the Raman spectra of the cyclopropane molecule have been studied by a number of authors.[1] The classification of the observed frequencies has recently been discussed by Linnett.[1] The symmetry properties and the selection rules for the normal vibrations are given in Table XCII and the assignments of the observed frequencies in Table XCIII.

Vibrations		Symmetry			Secletion rules	
Notation	Nature	class	σ_h	σ_v	Infrared	Raman
ν_1	ν_1 in CH_2	A'_1	s	s	ina.	p
ν_2	ν_2 in CH_2	A'_1	s	s	ina.	p
ν_3	ν_1 in C_3 ring	A'_1	s	s	ina.	p
ν_4	torsion of C_3 ring relative to the H_3 rings	A'_2	s	a	ina.	ina.
$\nu_5(2)$	ν_1 in CH_2	E'	s	deg.	⊥	d
$\nu_6(2)$	ν_2 in CH_2	E'	s	deg.	⊥	d
$\nu_7(2)$	bending of CH_2	E'	s	deg·	⊥	d
$\nu_8(2)$	$\nu_{2,3}$ in C_3ring	E'	s	deg.	⊥	d
ν_9	torsion of the two H_3 rings	A''_1	a	a	ina.	ina.
ν_{10}	ν_3 in CH_2	A''_2	a	s	∥	ina.
ν_{11}	tilting of CH_2	A''_2	a	s	∥	ina.
$\nu_{12}(2)$	ν_3 in CH_2	E''	a	deg.	ina.	d
$\nu_{13}(2)$	tilting of CH_2	E''	a	deg.	ina.	d
$\nu_{14}(2)$	twisting in CH_2	E''	a	deg.	ina.	d

Table XCII. Normal vibrations & selection rules of C_3H_6

In the infrared work, the dispersion obtained with the use of prism instruments is only moderate. The $\nu_5 \sim 3000$ cm^{-1} band is overlapped by the intense band $\nu_{10} \sim 3049$ cm^{-1}, and the $\nu_7 \sim 1022$ cm^{-1} band by the $\nu_{11} \sim 1041$ cm^{-1} band, their existence being revealed only by an asymmetry in the stronger bands. It would be desirable to examine the

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[1] Raman spectrum: Lespiau, Bourguel & Wakeman, Bull. Soc. Chim. 4, 51, 400, (1932); Kohlrausch & Köppl, Zeits. f. phys. Chem. B 26, 209, (1934); polarization data from Ananthakrishnan, Proc. Ind. Acad. Sci. 4, 82, (1936); Harris, Ashdown and Armstrong, J. Am. Ch. Soc. 58, 852, (1936).

Infrared spectrum: L. G. Bonner, Jour. Chem. Phys. 5, 704, (1937), 1.5—15μ; King, Armstrong & Harris, Jour. Am. Chem. Soc. 58, 1580, (1936), 0.8—10μ; J. W. Linnett, Jour. Chem. Phys. 6, 692, (1938), 1.5—25μ.

Assignment	Observed frequencies		Assumed freq.
	Infrared	Raman	
ν_1		2952 p	
$2\nu_2$ resonance	—	3010 p	
$4\nu_{14}$		3028 p	
ν_2	—	1454	
$2\nu_{14}$ resonance		1503 p	
ν_3	—	1187 p	
ν_4	—	—	1070
ν_5	ca. 3000		
ν_6	1435 *s*	1434	
ν_7	ca. 1022 *w*	1022	
ν_8	860 *s*	863	
ν_9	—	—	1000
ν_{10}	3049 *s*	—	
ν_{11}	1041 *s*	—	
ν_{12}	—	3080	
ν_{13}	—	?	1250
ν_{14}	—	740	
$\nu_{13}-\nu_8$		382	
$\nu_9+\nu_{14}$	1739 *m*		
$\nu_{11}+\nu_{14}$	1779 *w*		
$\nu_7+\nu_8$	1890 *s*	1873	
$\nu_4+\nu_7$	2083 *s*		
$\nu_6+\nu_{14}$	2179 *w*		
$\nu_2+\nu_8$	2331 *w*		
$\nu_2+\nu_7$ or $\nu_1+\nu_6$	2494 *w*		
$\nu_3+\nu_6$	2632 *w*		
$2\nu_6$		2856	
$\nu_1+\nu_8$, $\nu_5+\nu_8$	3846 *w*		
$\nu_5+\nu_{13}$, $\nu_8+\nu_5$	4200 *w*		
$\nu_2+\nu_5, \nu_5+\nu_6, \nu_1+\nu_6$, etc.	4450 *w*		
$\nu_5+2\nu_4, \nu_{12}+2\nu_7$, etc.	5128 *vw*		
$2\nu_5$, $2\nu_{12}$, etc.	6020 *w*		

Table XCIII. Vibrational spectrum of C_3H_6

absorption bands under higher dispersion and resolving power so that the distinction between the parallel and the perpendicular type bands can be made from the band contours.

From the three totally symmetrical vibrations, it is possible to determine the constants in the simple valence force potential

$$2V = 3k_1(\delta x)^2 + 6k(\delta r)^2 + 3k_\theta(r\delta\theta)^2, \tag{184}$$

where x is the C—C distance, r the C—H distance, and θ the H—C—H angle. The determinantal equation gives

$$\lambda_1+\lambda_2+\lambda_3=\left(\frac{1}{\mu}+\frac{1}{M}\cos\theta\right)k+2\left(\frac{1}{\mu}-\frac{1}{M}\cos\theta\right)k_\theta+\frac{3}{M}k_1,$$

$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1=\frac{3}{mM}(k+2k_\theta)\,k_1+\frac{2(M+2m)}{m^2M}\,k\,k_\theta$$

$$\lambda_1\lambda_2\lambda_3=\frac{6}{m^2M}k\,k_1\,k_\theta\,, \tag{185}$$

where $\mu=mM/(M+m)$. With the values $\nu_1\sim3000$, $\nu_2\sim1485$, and $\nu_3\sim1187$ cm^{-1}, one obtains

$$k_{CH}=4.85, \qquad k_{CC}=5.17,^{2} \qquad k_\theta=0.44. \tag{186}$$

§8. Ten-atomic Molecules

1) Dimethyl acetylene $C_2(CH_3)_2$

The structure of this molecule can be expected to be like that of ethane with the difference that there are two more C atoms between the two CH_3 groups. Since the H atoms in the two groups are much farther apart than they are in ethane, it is very probable that the two CH_3 groups are more or less free to rotate with respect to each other about the axis of symmetry. In any case, the symmetry properties of the normal vibrations will be those given in Table LXXX for the ethane molecule. There are 4 totally symmetrical vibrations of the A_1 class; 3 parallel vibrations of the class A_2; 4 doubly degenerate vibrations of the class E (or E' or E_u); 4 doubly degenerate vibrations of the class $\bar{E}$ (or E'' or E_g); and one degree of freedom for the internal rotation (or torsional oscillation). These make up the 24 vibrational degrees of freedom for the molecule. The selection rules for these normal vibrations are given in Table LXXX.

The nature of these normal vibrations can be roughly described as follows. Of the 4 Raman effect active A_1 vibrations, one is mainly determined by the $C\equiv C$ bond, one by the $C-C$ bond, one by the valence vibration $\nu_1(1)$ in the CH_3 group, and one by the deformation vibration

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[2] The value 5×10^5 obtained here for the C—C bond constant is to be compared with the value 4.0×10^5 obtained by L. G. Bonner, Jour. Chem. Phys. 5, 293, (1937), by treating the cyclopropane molecule as an equilateral triangle with particles of mass 14 at the vertices. This difference shows that neglecting the coupling of the motions of the C and the H atoms leads to too low a value for the C—C bond constant, and that such a calculation cannot be used to obtain accurate values of potential constants in general.

$\nu_3(1)$ in the CH_3 group. The 3 parallel, infrared active vibrations are the out-of-phase vibrations of the last 3 mentioned above. Of the 8 doubly degenerate vibrations, 2 are essentially the in-phase and out-of-phase valence vibrations $\nu_2(2)$ in the CH_3 groups, 2 arise from the deformation vibrations $\nu_4(2)$ in the CH_3 groups; and 4 arise from the bending of the linear six-particle molecule (H_3)-C-C-C-C-(H_3) similar to the diacetylene C_4H_2 molecule. These approximate considerations will furnish a guide for the assignment of the fundamental frequencies.

The 7 parallel vibrations can be easily treated by the normal coordinate method. We shall assume the modified valence force potential

$$2V = k_1(\delta R)^2 + 2k_2(\delta r_c)^2 + 6k_\Theta(r\delta\vartheta) + 6k_\varphi(s\delta\varphi)^2 + 6k(\delta r)^2$$
$$+ 4k_3(\delta R)(\delta r_o) + 12k_4(\delta r_c)(s\delta\varphi), \tag{187}$$

in which R is the C $\equiv$ C distance, r_o the C$-$C distances, r the C$-$H distances, ϑ the H$-$C$-$H angle, and φ the H$-$C$-$C angle. The determinantal equation gives for the four totally symmetrical vibrations

$$\sum^4 \lambda_i = \frac{1}{M}\left[A\,k + B\,k_\alpha + 2(k_1 + k_2 - 2k_3) - 6\sin\varphi\,k_4\right],$$

$$\sum_{i\neq j} \lambda_i\lambda_j = \frac{2}{M^2}\Big[(k_1k_2 - 2k_3^2) + (Ak + Bk_\alpha)(k_1 - 2k_3) + (Ck + Dk_\alpha)k_2$$
$$+ \frac{M(M+3m)}{2m^2}kk_\alpha - 3\sin\varphi\left(\frac{M}{m}k + 2k_1 - 2k_3\right)k_4 - 3Dk_4^2\Big],$$

$$\sum \lambda_i\lambda_j\lambda_k = \frac{2}{mM^2}\Big[(k + k_\alpha)(k_1k_2 - 2k_3^2) + \frac{M+3m}{m}(k_1 - 2k_3)kk_\alpha +$$
$$\frac{2M+3m}{2m}kk_2k_\alpha + 6\sin\varphi(k_1 - k_3)kk_4 - 3\left(\tfrac{1}{2}k_1 + \frac{2M+3m}{2m}k\right)k_4^2\Big],$$

$$\lambda_1\lambda_2\lambda_3\lambda_4 = \frac{2}{m^2M^2}\left[k_\alpha(k_1k_2 - 2k_3^2) - 3k_1k_4^2\right]k \tag{188}$$

where

$$k_\alpha = k_\varphi + k_\Theta(r/s)^2\,\frac{12.\cos^2\varphi}{1+3\cos^2\varphi},$$

$$A = \frac{M}{m} + 3\cos^2\varphi,\quad B = \frac{M}{m} + 3\sin^2\varphi,\quad C = \tfrac{1}{3}\left(A + \frac{M}{m}\right),\quad D = \tfrac{1}{3}\left(B + \frac{M}{m}\right)$$

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[1] The determinantal equaion for the parallel vibrations has been given by G. Glockler & F. T. Wall, Jour. Chem. Phys. 5, 813, (1937), for a simple valence force potential, viz., $k_4 = k_3 = 0$ in (187).

The equations for the antisymmetrical vibrations ν_5, ν_6, ν_7 can be obtained from these by setting $k_1=k_3=0$. From the four Raman and the three infrared frequencies, it should be possible to determine the seven constants (of which k_Θ and k_φ appear only in combinations) in the potential (187). The treatment of the degenerate vibrations is too complicated to be given here; but when one's interest is mainly in the valence bond constants, the above relations are sufficient.

The Raman spectrum of dimethyl acetylene was studied by Glockler, Davis and Renfrew. No infrared spectrum data seem to have been given. The following table summarizes the Raman spectrum data and their tentative interpretations on the basis of the foregoing considerations.

Suggested assignment	Raman frequencies (liquid)		
ν_8 ? E	213	(1b)	
ν_{12} $E(\delta$ in $C-C\equiv C-C)$	374	(5b)	
774−374 or ν_9 E	400	(0b)	
ν_{13} $E(\delta$ in $CH_3-C\equiv C-CH_3)$	687	(3b)	
$2\nu_{12}$	697	(4s)	
ν_1 $A_1(C-C)$	773.5	(4s)	
$2\nu_9$	788.5	(3s)	
	1029	(3s)	
	(1243)	(0b)	
ν_4 $A_1(\delta$ in $CH_3)$	1379	(5b)	
ν_{11} or ν_{15} $E(\delta$ in $CH_3)$	1447	(4b)	
ν_2 in mol. with C^{13}	2201.4	(1s)	
$3\nu_1$	2280.2	(1s)	
ν_2 $A_1(C\equiv C)$	2234.6	(6s)	
$3\nu_1$	2312.6	(6s)	
$2\nu_4$	2736.8	(2s)	
$2\nu_{11}$, $2E(\delta$ in $CH_3)$	2861.8	(4s)	
ν_3 $A_1(CH_3)$	2920	(7s);	2938 in gas
ν_{10} or ν_{14} $E(\nu$ in $CH_3)$	2961	(3b)	

Table XCIV. Raman spectrum of $C_2(CH_3)_2$. Numbers in parentheses give the relative intensities, "b", "s" means the line is broad or sharp respectively.

On intensity and order of magnitude considerations, the assignments of the totally symmetrical vibrations seem to be quite definite.

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[2] G. Glockler and H. M. Davis, Jour. Chem. Phys. 2, 881, (1934); Glockler and F. T. Wall, Phys. Rev. 51, 529, (1937), gaseous $C_2(CH_3)_2$; Glockler and M. M. Renfrew, Jour. Chem. Phys. 6, 408, (1938), made some corrections to the interpretation given in the first paper. The modes of vibrations given by the first paper seem to be not quite correct, for 8 frequencies were assigned to parallel vibrations while there can be only 4 such fundamentals.

The appearance of two intense lines at 2234 and 2313 cm^{-1} can be understood from a resonance interaction between the A_1 ($C \equiv C$) fundamental and the second harmonic of the A_1 ($C-C$) fundamental. Similarly, the two lines at 2862 and 2920 cm^{-1} can be ascribed to the resonance between the A_1 $\nu_3(CH_3)$ fundamental and the first harmonic of the deformation vibrations in the CH_3 groups in either the A_2 or the E class. The assignments of the degenerate fundamentals are less certain as the observed weaker lines may not be all fundamentals while some of the fundamentals may not have appeared because of low intensities. A study of the infrared spectrum must be most useful for ascertaining the fundamental frequencies and hence the potential energy of the molecule.

As the three infrared active parallel fundamentals ν_5, ν_6, ν_7 are not known, it is not possible to determine the six constants in (187). In a first approximation obtained by neglecting the terms k_3 and k_4, and with

$$\nu_1 = 773.5, \qquad \nu_2 = 2274, \qquad \nu_3 = 2920, \qquad \nu_4 = 1379\, cm^{-1},$$

we obtain

$$k_{C-H} = 4.70, \qquad k_{C-C} = 6.8, \qquad k_{C\equiv C} = 14.4, \qquad k_{\alpha} = 0.92. \qquad (189)$$

These values are very rough, since the terms in k_3 and k_4 have been neglected and since the frequencies are obtained for the liquid and have not been corrected for the anharmonicity. The $C-C$ and $C\equiv C$ bond constants differ, however, enough from their values in C_2H_6 and C_2H_2, *viz.*, $k_{CC}=4.5$ in (183) and $k_{C\equiv C}=17$ in (58), to suggest some double bond contributions as the result of reasonance. Recent electron diffraction measurements give for the bond distances $r(C\equiv C)=1.195$Å and $r(C-C)=1.474$Å in dimethyl acetylene.[3] The smaller distance in $C-C$ compared with the pure single bond distance 1.53Å indicates some double bond character, in agreement with the above evidence.

§9. Twelve-atomic Molecules

The number of twelve-atomic molecules, especially in organic chemistry, is enormously large, and of these there is quite a large number whose Raman spectra have been studied. Such spectra can be expected to be very complicated. Only a few molecules, however, have high enough symmetries to permit a complete analysis of the vibrational spectra. For this reason, we shall only consider the benzene molecule and some of its derivatives.

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[3] L. Pauling, H. D. Springall & K. J. Palmer, Jour. Am. Chem. Soc. 61, 927, (1939).

The structure of the benzene ring is one of the most important problems in organic chemistry. Simply speaking, the problem is to obtain a structural formula, *viz.*, the arrangement of the nine C–C valence bonds, that accounts for the special stability of the ring. Various formulae have been proposed, but a clear understanding was not obtained until the concept of quantum mechanical resonance was applied. It was shown by Pauling and Wheland[1] that as the result of the resonance among the five structures

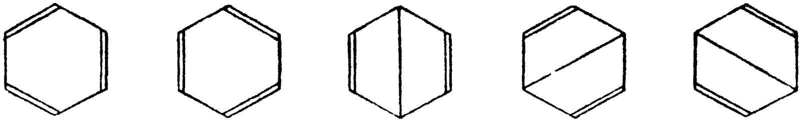

Fig. 38. Canonical structures of benzene molecule

the wave function of the normal state of the benzene molecule is a linear combination of the wave functions of the five structures, *viz.*,

$$\psi = 0.6216\,(\psi_{\mathrm{I}} + \psi_{\mathrm{II}}) + 0.2711\,(\psi_{\mathrm{III}} + \psi_{\mathrm{IV}} + \psi_{\mathrm{V}}). \qquad (190)$$

We shall not enter into the question concerning the increased stability of the molecule arising from this resonance. Suffice it to say that the wave function above gives a hexagonally symmetrical structure for the normal electronic state in complete agreement with the vibrational spectrum data, as we shall see below.

1) C_6H_6 (benzene), 1a) C_6D_6

The infrared and the Raman spectra of the benzene molecule have been studied by a large number of workers. The observed data have been summarized by Kohlrausch[1] and by Angus, Ingold *et al*[2]. The symmetry properties and selection rules for the normal vibrations of the molecule have been obtained by Wilson[3] by the method of the group theory. He also gave a normal coordinate treatment of the normal vibrations with the use of a potential of the valence force type containing six constants, namely,

[1] L. Pauling, & G. W. Wheland, Jour. Chem. Phys. 1, 362, (1933), and other references given in footnote (3) in §5, A, Chap. III. Also see W. G. Penney, *The Quantum Theory of Valence*, Methuen, 1935.

[1] K. W. F. Kohlrausch, Phys. Zeits. 37, 58, (1936).

[2] W. R. Angus, C. K. Ingold & A. H. Leckie, Jour. Chem. Soc. Lond. P. 929, (1936); Bailey, Hale, Ingold & Thompson, *ibid.*, P. 931, (1936); Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson & Wilson, *ibid.*, 936, (1936).

[3] E. B. Wilson, Jr., Phys. Rev. 45, 706, (1934).

$$2V = K\Sigma(\delta R)^2 + q\Sigma(\delta r)^2 + H(b-a)^2\Sigma(\delta\lambda)^2 + h(b-a)^2\Sigma(\delta\mu)^2$$
$$+ ka^2\Sigma(\delta\gamma)^2 + \varkappa c^2\Sigma(\delta\varphi_{ij})^2, \qquad (191)$$

where R, r are the C—C and C—H bond distances, $\delta\lambda$ and $\delta\mu$ are the bendings of the C—H bonds in and out of the plane of the molecule respectively, $\delta\gamma$ the changes in the C—C—C angles, and the terms in $\varkappa$ give the potential energy for the twisting of the C—C bonds when the C atoms move out of the plane of the molecule. a and b are the distances of the C and the H atoms, respectively, from the center of the hexagon, and $c = \frac{\sqrt{3}}{2}a$. We shall refer to Wilson's paper for the equations giving the normal frequencies in terms of the potential constants in (191). It has been found that the potential (191) is very successful when applied to the observed frequencies, in spite of the small number of constants it contains.

In Table XCV are given the symmetry classes and the selection rules of the normal vibrations of both the D_{6h} (benzene and benzene-d_6) and the D_{3h} (1-3-5 benzene-d_3 and substituted derivatives) models. The modes of the normal vibrations are shown in Wilson's paper.

Notation	D_{6h}				D_{3h}			
	Sym. class	No. of Vib's	Infra.	Ram.	Sym. class	No. of Vib's	Infra.	Raman
ν_1, ν_2	A_{1g}	2	—	p	A'_1	4	—	p
ν_{12}, ν_{13}	B_{1u}	2	—	—				
ν_6, ν_7, ν_8, ν_9	E_{2g}	4	—	d	E'	7	act.	d
ν_{18}, ν_{19}, ν_{20}	E_{1u}	3	act.	—				
ν_3	A_{2g}	1	—	—	A'_2	3	—	—
ν_{14}, ν_{15}	B_{2u}	2	—	—				
ν_{10}	E_{1g}	1	—	d	E''	3	—	d
ν_{16}, ν_{17}	E_{2u}	2	—	—				
ν_{11}	A_{2u}	1	act.	—	A''_2	3	act.	—
ν_4, ν_5	B_{2g}	2	—	—				

Table XCV. Normal vibrations of benzene & benzene-d_6

The assignments of the fundamental frequencies have been discussed by Angus *et al*[2] and by Lord and Andrews[4]. They agreed in the assignments of the Raman and infrared active frequencies; but differed somewhat in the calculated frequencies of the completely inactive frequencies. From considerations of the specific heat of crystalline benzene, it was found that the frequencies, especially of the two low frequency fundamentals, given by Lord and Andrews are correct.[5] Hence in Table XCVI we give only the assignments of Lord and Andrews of C_6H_6 and C_6D_6 and the constants of the potential (191) with which the calculated frequencies are obtained. It is seen that the agreement between the observed and the calculated frequencies is very good.

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[4] R. C. Lord & D. H. Andrews, Jour. Phys. Chem. 41, 149, (1937).

Vib'n		C_6H_6 Infra.	C_6H_6 Raman	C_6H_6 Calc.	C_6D_6 Infra.	C_6D_6 Raman	C_6D_6 Calc.
A_{1g}	ν_1	—	992 p	993	—	945 p	
	ν_2	—	3061 p	3061	—	2292 p	
B_{1u}	ν_{12}	—	—	1008	—	—	965
	ν_{13}	—	—	3063	—	—	2285
E_{2g}	ν_6	—	606 d	608	—	577	
	ν_9	—	1178 d	1170	—	867	
	ν_8	—	1596 d	1645	—	1559	
	ν_7	—	3047 d	3107	—	2264	
E_{1u}	ν_{18}	1037	—	1030	813	—	
	ν_{19}	1485	—	1480	1333	—	
	ν_{20}	3080	—	3080	2294	—	
A_{2g}	ν_3	—	—	1190	—	—	950
B_{2u}	ν_{15}	—	—	1145	—	—	785
	ν_{14}	—	—	1854	—	—	1830
E_{1g}	ν_{10}	—	850	850	—	661	
E_{2u}	ν_{16}	—	(406)	406	—	—	316
	ν_{17}	—	—	1160	—	—	1063
A_{2u}	ν_{11}	671	—	783	503	—	
B_{2g}	ν_4	—	—	538	—	—	504
	ν_5	—	—	1520	—	—	1002

$K_{OO} = 7.58$, $k = 0.65$, $H = 0.76$, $q_{OH} = 5.05$,

$\varkappa = 0.23$, $h = 0.34 \times 10^5$.

Table XCVI. Fundamental frequencies & potential constants of C_6H_6 & C_6D_6

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[5] Lord, J. E. Ahlberg & Andrews, Jour. Chem. Phys. 5, 649, (1937). The observed specific heats of solid benzene agree completely with the calculated values with the fundamentals given in Table XCVI for the whole temperature range from 4°*K* to 260°*K*. Early observations on the electronic bands (absorption) show a frequency difference of 160 cm^{-1}. This was thought at first to be the ν_{16} fundamental of the normal electronic state. Recent study of the electronic bands by Sponer, Nordheim, Sklar & Teller, Jour. Chem. Phys. 7, 207, (1939), establishes, however, the frequency $\nu_{16} \sim 400$ cm^{-1}.

The potential constant obtained for the C$-$C bond is of special interest. Its value 7.58×10^5 lies between the value for the double bond 9.7×10^5 (see 163 and 164) and the value 5.57×10^5 in (183) for the single bond. Thus the effect of the quantum mechanical resonance also manifests itself in the bond constant K.

A large number of infrared bands and Raman lines has been observed for both C_6H_6 and C_6D_6 in addition to those given in Table XCVI. They have been summarized by Angus *et al*[2]. Their assignments are, however, not quite definite because of the closeness between certain fundamentals and hence of the possibility of making more than one assignments to certain observed frequencies. For this reason we shall not include these harmonic and combination bands here.

An interesting feature in the spectrum of the benzene molecule is that the Raman line at 992 cm^{-1} due to the totally symmetrical vibration ν_1 is accompanied by 4 satellites at 979, 984, 999 and 1005 cm^{-1}.[2] The line at 984 cm^{-1} was ascribed to the molecule $C_5^{12}C^{13}H_6$ by Gerlach[6]. Quantitative measurements of the relative intensities of the 984 and 992 cm^{-1} lines have been made by Cheng, Heueh and Wu[7] and by Rao[8]. They all found the value 6:100 for the ratio of the intensities of these two lines, in agreement with the value expected from the relative abundance ratio of the isotopes C^{13} and C^{12}. The observed isotope shift, namely, *ca*, 8.2 cm^{-1},[7] does not agree with the theoretical value of 6.3 cm^{-1} within the limit of accuracy of the measurements. Langseth and Lord[9] suggested that this discrepancy may be due to a depression of the level ν_1 in $C_5^{12}C^{13}H_6$ by this amount ($8.2-6.3=1.9$ cm^{-1}) as a result of the resonance interaction between ν_1 and ν_{12} at *ca*. 1003 cm^{-1}. This resonance will raise ν_{12} by 1.9 cm^{-1} and impart some intensity of ν_1 to ν_{12} (*i.e.*, the wave function of the level ν_{12} will contain some contribution of the wave function of ν_1). The ratio of the intensities of ν_{12} and ν_1 can be calculated by the method of §4, B), Chap. III, to be *ca*. 1:10.[10] On this explanation of the satellite at 1005 cm^{-1}, the ratio of the intensities of 984 and 992 lines should be 5.5:100 compared with the observed value 6:100.

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[6] W. Gerlach, Sitz. Math.-Nat. Bayer Akad. München, 39, Nr. 1, (1932).

[7] H. C. Cheng, C. F. Hsueh & T. Y. Wu, Jour. Chem. Phys. 6, 8, (1938).

[8] B. S. R. Rao, *ibid.*, 6, 343, (1938).

[9] A. Langseth R. C. Lord, *ibid.*, 6, 203, (1938).

[10] For resonance which is not close, *i.e.*, $y=\frac{\Delta}{|b|}\ll1$, the ratio of the intensities is given by $(\sqrt{\Delta^2+2b^2}-\Delta)/(\sqrt{\Delta^2+2b^2}+\Delta)$ instead of $\alpha^2:\beta^2$ in (120), Chap. III.

The other two satellites at 979 and 999 cm^{-1} are explained by Langseth and Lord as arising from transitions from ν_6 to the two resonating levels ν_8 and $\nu_1+\nu_6$.[11] The expected intensities of these two lines on consideration of the Boltzmann factor are given in Table XCVII.

In C_6D_6, the same authors observed only two satellites at 939.5 and 962.1 cm^{-1} for the totally symmetrical vibration at 945 cm^{-1}. These two lines correspond to the ν_1 and ν_{12} of $C_5^{12}C^{13}D_6$. The other two satellites in C_6H_6 are not observed because $\nu_1+\nu_6-\nu_6$ coincides with the main line $\nu_1=945$ and the transition $\nu_8-\nu_6$ has vanishingly small intensity since the levels ν_8 and $\nu_1+\nu_6$ are not in resonance as in the case of C_6H_6. The intensities of the two lines at 939.5 and 962.1 cm^{-1} observed and calculated as before are given below.

		C_6H_6			C_6D_6	
	Obs.ν	Obs.I (7,8)	Calc.I	Obs.ν	Obs.I (9)	Calc.I
$\nu_8-\nu_6, \nu_1+\nu_6-\nu_6$	979		5.1			
$\nu_1(C_5^{12}\,C^{13}H_6)$	984	6	5.5	939.5	10	5.8
ν_1	992	100	100	945.2	100	100
$\nu_8-\nu_6, \nu_1+\nu_6-\nu_6$	999		5.9			
$\nu_{12}\,(C_5^{12}C^{13}H_6)$	1005		0.5	962.1	0.1	0.2

Table XCVII. Fine structure of the ν_1 lines of C_6H_6 & C_6D_6

2) Deuterated benzenes

The spectra of the partially deuterated benzenes have been studied by a number of authors[1]. The dideuterobenzene and the tetradeuterobenzene have three isomers, namely, the *ortho*, *meta* and *para* forms. Trideuterobenzene has also three forms, namely, the *mes*, *vic* and *sym* forms. As the symmetry of the C_6H_6 molecule is lowered by the substitution of deuterium atoms, certain inactive frequencies become active in absorption or in the Raman effect or in both, and certain degenerate frequencies may split into nondegenerate frequencies. A knowledge of the spectra of these molecules will throw more light on the potential function of the C_6H_6 molecule. The data available now are, however, still rather incomplete for an assignment of all the fundamental frequencies of these molecules. We shall only give the assignment of the fundamental frequencies of the symmetrical trideuterobenzene (1-3-5 benzene-d_3) for which the selection rules have been given in Table XCV.

---

[11] In C_6H_6, there are two depolarized lines at 1584.8 and 1606.4 cm^{-1}. These are due, according to E. B. Wilson, to transitions from the normal state to the resonance levels ν_8 and $\nu_1+\nu_6$. The value 1596 cm^{-1} given for ν_8 in Table XCVI is estimated from the two observed lines.

[1] A. Langseth & R. C. Lord, Danske Vidensk. Selskab. Math. Fys. Meddelelser. 16, 6, (1938); A. Klit & A. Langseth, Jour. Chem. Phys. 5, 925, (1937); C. K. Ingold, Proc. Roy. Soc. A 169, 149, (1938).

Vibration		Infrared	Raman
A'_1	ν_1	—	954 *s*
	ν_2	—	
	ν_{12}	—	1001 *s*
	ν_{13}	—	
E'	ν_6	591 *w*	590 *m*
	ν_9	1098 *w*	1102 *m*
	ν_8	1573 *w*	1572 *s*
	ν_7		
	ν_{18}	833 *s*	831 *m*
	ν_{19}	1407 *s*	1407 *w*
	ν_{20}		
A_2	ν_3	—	—
	ν_{15}	—	—
	ν_{14}	—	—
E''	ν_{10}	—	707 *m*
	ν_{16}	—	375 *w*
	ν_{17}	—	1080 *w*
A''_2	ν_{11}	533 *s*	—
	ν_4	?	—
	ν_5	914 *s*	—

Table XCVIII. Fundamental frequencies of sym. $C_6H_3D_3$

The assignment in Table XCVIII is guided by considerations of the selection rules and the corresponding frequencies in C_6H_6 and C_6D_6 in Table XCVI. The greater separation between ν_1 and ν_{12} in *sym.* $C_6H_3D_3$ compared with that in C_6H_6 (47 cm^{-1} compared with 18 cm^{-1}) is explained by Klit and Langseth[2] as arising from resonance interaction between the two levels in *sym.* $C_6H_3D_3$ (no resonance interaction occurs in C_6H_6 since ν_1 and ν_{12} have different symmetry characters).

3) $B_3N_3H_6$ (triborine triamine)

The structure of this molecule is shown by electron diffraction measurements to be similar to that of the benzene molecule.[1] The Raman and the infrared spectra of the molecule have recently been investigated by Crawford and Edsall[2] who also give a classification of the observed frequencies and a normal coordinate treatment of the normal vibrations, which is similar to that of Wilson for the C_6H_6 molecule. The potential employed is similar to (191), except that the terms in q, H, h are to be replaced by $q_{BH}, q_{NH}, H_{BH}, H_{NH}, h_{BH}, h_{NH}$ respectively for the N−H and the B−H bonds. The fundamental frequencies and the potential constants obtained by these authors are given in Table IC.

---

[2] Klit & Langseth, *loc. cit.*, suggested that the greater separations between ν_1 and ν_{12} in meta $C_6H_4D_2$ and $C_6H_2D_4$ (symmetry C_{2v}) and sym. $C_6H_3D_3$ (symmetry D_{3h}) compared with the ortho $C_6H_4D_2$ and $C_6H_2D_4$ are due to resonance interactions which occur in molecules having the correct symmetries such as the above.

[1] A. Stock & R. Wierl, Zeits. f. Anorg. Chem. 203, 228, (1931), gave from X-ray diffraction measurements $r(B-N)=1.47\pm0.07$ Å. More recently, S. H. Bauer, Jour. Am. Chem. Soc. 60, 524, (1938), gave from electron diffraction measurements $r(B-N)=1.44\pm0.02$ Å.

Vibration		Infrared	Raman
A_1'	ν_1	–	851 (6) p
	ν_2	–	2535 (9) p
	ν_{12}	–	938 (7) p
	ν_{13}	–	3450(10) p
E'	ν_6	525 (20)	519 (3) d
	ν_9	917(100)	
	ν_8	1610 (30)	
	ν_7	2519 (60)	
	ν_{18}	717 (70)	717 (1)
	ν_{19}	1466 (85)	1465 (1)
	ν_{20}	3400 (5)	
A_2'	ν_3	–	– (1110)
	ν_{15}	–	– (800)
	ν_{14}	–	– (1650)
E''	ν_{10}	–	798 (2)
	ν_{16}	–	288 (2)
	ν_{17}	–	1070 (5) d
A_2''	ν_{11}	622(30)	–
	ν_4	415(40)	–
	ν_5	1098(40)	–

$K_{BN}=6.30$, $k = 0.53$, $H_{BN}=0.35$, $H_{NH}=0.65$,

$q_{BH}=3.42$, $q_{NH}= 6.52$, $\varkappa =0.10$, $h_{BH}=0.23$, $h_{NH}=0.42$.

Table IC. Fundamental frequencies & potential constants of $B_3N_3H_6$

In Table IC, the classification is based on considerations of the selection rules given in Table XCV (symmetry D_{3h}) and the frequencies of the corresponding vibrations in C_6H_6. The three totally inactive frequencies given in parentheses are the calculated values obtained with the potential constants given in the table. Comparisons of the frequencies and potential constants in $B_3N_3H_6$ and C_6H_6 show that the parallelism is most striking.

---

[2] B. L. Crawford & J. T. Edsall, Jour. Chem. Phys. 7, 223, (1939).

With the fundamentals in Table IC, the other observed infrared and Raman frequencies can be satisfactorily accounted for, as shown in Table C.

Assignment	Infrared	Raman
$2\nu_{16}$	570 (5)	
$\nu_{17}-\nu_{16}$	778(30)	
$\nu_5-\nu_{16}$	790 (5)	
$\nu_{16}+\nu_{18}$	990(40)	
$\nu_9+\nu_{16}$	1199(35)	
$\nu_{12}+\nu_{16}$		1228 (?)
$\nu_1+\nu_6$		1370 (1)
$2\nu_{18}$	1410(30)	
$\nu_9+\nu_{12}$	1850(30)	1843 (?)
$\nu_{18}+\nu_{19}$	2174(10)	

Table C. Harmonic & combination bands of $B_3N_3H_6$

§10. Summary of Molecular Constants

In the following table, we shall summarize the bond constants and bond distances of a few chemical bonds of common occurrence. The bond distances marked with * are obtained from electron diffraction measurements; those unmarked are the spectroscopic values. It is to be emphasized that one must not attach too much significance to the exact numerical values of the bond force constants since (i) their values depend on the form of the potential function employed, and with potentials of the same force type, on whether certain cross terms (interaction terms) are included, and (ii) corrections of the observed frequencies for anharmonicity cannot be made in all cases. In spite of these, however, it can be seen from the table that both the bond constants and the bond distances agree, qualitatively, in indicating the nature of the bonds (with respect to the presence or absence of quantum-mechanical resonance). A quantitative calculation of the various bond contributions in the case of resonance from the bond force constants cannot be made as from the bond distance bond type relations of Pauling, Brockway and Beach,[1] on account of the uncertainties of the bond constants as mentioned above. Nevertheless they furnish us with corroborative informations in many cases.

---

[1] Pauling, Brockway & Beach, Jour. Am. Chem. Soc. 56, 2706, (1935).

	C–H								
Molecule	–CH_3	=CH_2	≡CH	C–C	C=C	C≡C	C–O	C=O	C≡O
C_2H_6	4.85			4.5–5.5 * (1.52)					
CH_4	5.1	(1.09)							
CH_3X	5.0								
$CHCl_3$	5.1								
H_3C–C_2H	4.8		5.75	6.25(1.463)		14.5(1.198) *			
$C_2(CH_3)_2$	4.7			6.8 (1.474) *		14.6(1.198) *			
H_3C–CN	4.9			5.2 (1.55) *					
H_3C–NC	4.9								
H_3C–OH	4.8								
C_6H_6	5.0			7.6(1.39) *					
C_2H_4		5.2(1.08)			9.8(1.33)				
OCH_2		4.2						12.(1.15) *	
$OCCH_2$		4.8(1.07)			9.8(1.35) *			12.(1.17) *	
$C(CH_2)_2$		4.9			9.5(1.31) *				
C_3H_6		4.9		5.2 (1.53) *					
HCN			6.2(1.057)						
C_2H_2			6.2(1.057)			17. (1.199)			
C_4H_2			6.0	3.6 (1.36) *		16.3(1.187) *			
C_2N_2				6.7 (1.37) *					
C_2Cl_4				6.8 (1.38) *					
OCN^-							4.7		
$CO_3^=$							6.2		
CO_2									15.9(1.15)
C_3O_2					12.5(1.29) *				16.0(1.20)
OCS								13.4(1.16)	

	C≡N	C–F	C–Cl	C–Br	C–I
SCN^-	14.4				
$SeCN^-$	14.6				
HCN	16.5(1.154)				
C_2N_2	17.5(1.155) *				
H_3C–CN	17.0(1.16) *				
H_3C–NC	16.0(1.17) *				
XCN	16.7(1.13) *		5.2(1.67) *	4.2(1.79) *	2.9(1.96) *
C_2Cl_4			4.5(1.73) *		
$C_2H_2Cl_2$(trans)			4.0(1.69) *		
CH_3X		5.8(1.39) *	3.5(1.77) *	2.8(1.91) *	2.2(2.28) *
CX_4		3–5.4(1.36) *	1.9(1.76) *	1.4(1.93) *	(2.14) *

Table CI. Force constants and distances of C–H, C–C, C–O, C–N, C–X bonds. Bond distances are given in parentheses. X stands for F, Cl, Br, or I.

NOTES ADDED IN PROOF (NOV. 1939)

When the foregoing pages are in the press, a number of papers on molecular spectra has appeared. The following gives a few of these papers on subjects discussed in this work.

Chap. IV, §4, A. Interaction between vibration and rotation. Besides the papers mentioned in footnotes (6)—(9) on P. 135, a recent paper by W. H. Shaffer and H. H. Nielsen, Phys. Rev. 56, 188, (1939), deals with the problem of the energy of a vibrating-rotating triangular YX_2 molecule.

Chap. V. P. 191, NH_3
Z. I. Slawsky and D. M. Dennison, Jour. Chem. Phys. 7, 509, (1939), have obtained the energy change due to centrifugal distortion of the axially symmetrical molecules YX_3 and ZYX_3 in terms of the quantum numbers J, K and the molecular constants. The formulas for the pure rotational spectra of NH_3 and ND_3 are, respectively,

$$\nu = 2B_0J + 0.00160J - 0.00250J^3 + 0.00190K^2J,$$

$$\nu = 2B_0J + 0.000452J - 0.000704J^3 + 0.000522K^2J.$$

These justify the empirical expressions given on P. 195 and P. 199. The term in K^2J predicts a fine structure splitting of each line corresponding to different values of K ($\Delta K=0$), but the splitting is too small to be observed except for very high menbers of the series.

Chap. V. P. 205, BF_3
The infrared spectrum of BF_3 has been recently measured under higher dispersion by D. M. Gage and E. F. Barker, Jour. Chem. Phys. 7, 455, (1939). The band centers are given as

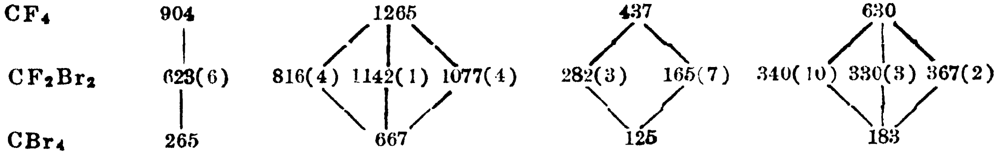
	ν_1	$\nu_2 \perp$	$\nu_3 \parallel$	$\nu_4 \perp$
$B^{11}F_3$	888 (*Ra*)	1446	691.5	480.5
$B^{10}F_3$	888 (*Ra*)	1497	719.8	482.1

The parallel band ν_3 has been resolved, and from the rotational line spacings, the moment of inertia about the symmetry axis is found to be 79× 10^{-40} and the B−F distance 1.29 Å.

Chap. V. P. 237. Methyl halides
The work of Z. I. Slawsky and D. M. Dennison mentioned in footnote 3 has now appeared in Jour. Chem. Phys. 7, 522, (1939). They showed that the observed frequencies of the methyl halides in Table IL can be reproduced by employing the following values for the constants in the potential (136) on P. 237.

	$k_{C\text{-}H}$	k_ϑ	k_φ	$k_{C\text{-}X}$	k_4
CH_3F	4.878	0.443	0.8097	6.09	0.713
CH_3Cl			0.596	4.417	0.725
CH_3Br			0.536	4.193	0.775
CH_3I			0.463	3.292	0.562

Chap. V. P. 250, CF_2Br_2
The Raman spectrum of CF_2Br_2 has been recently given by G. Glockler and G. R. Leader, Jour. Chem. Phys. 7, 553, (1939). In the absence of polarization data, we suggest the following tentative assignments (see diagram 140, P. 245).



Chap. V. P. 303, Question of internal rotation in C_2H_6
In a recent paper, E. Gorin, J. Walter and H. Eyring, Jour. Am. Chem. Soc. 61, 1878, (1939), have shown by a wave mechanical calculation that a high potential barrier of the order 3000 cal/mole between the D_{2h} and the D_{3d} configurations in C_2H_6, with the D_{3h} more stable, can be understood on considering the combined effect of the interactions between the H atoms and the hybridized C−C orbitals and the contributions from double bond characters. They showed, on the other hand, that the induction effect proposed by Eucken and Schäfer (footnote 8 on P. 303) is too small to account for the value 3000 cal./mole. On the basis of this

theory of Gorin *et al*, the suggestion of Wu on P. 311 for the existence of a potential minimum at the *cis* configuration of the 1,2 dihalogen ethanes finds some justificaiton.

Chap. V. P. 315, Dimethyl acetylene
The infrared spectrum of dimethyl acetylene has recently been measured by B. L. Crawford, Jour. Chem. Phys. 7, 555, (1939), who also measured the depolarization of the Raman lines. The fundamental frequencies are, with the notations of Table LXXXII, P. 296,

A_1	725	1380	2270	2918	(Raman)
A_2		1126	1380	2976	(Infra)
E	371	1029	1448	2961	(Raman)
E	(213)	1050	1468	2976	(Infra)

Two of the Raman effect active fundamentals differ from the observed values in Table XCIV because of corrections for resonance interactions. From measurements of the specific heat of the molecule, B. L. Crawford and W. W. Rice, Jour. Chem. Phys. 7, 437, (1939), concluded that the torsional degree of freedom is one of almost free rotation, the restricting potential barrier not exceeding 500 cal/mole.

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SUPPLEMENT

Since the publication of the present volume in 1939, numerous investigations on the infrared and the Raman spectra of polyatomic molecules have been carried out. In the following pages, references to the recent literature and some brief discussions in certain cases are given. A table summarizing the best molecular constants now available is given at the end of this supplement, to replace Table CI on P. 327. With the space available and on account of the inaccessibility of the writer to the literature since 1941, it has not been possible to make a fuller discussion, nor to quote all the original papers bearing on the subject. These limitations, however, are rendered less serious by the appearance of the detailed and critical resume by Dennison in the Review of Modern Physics, vol. 12, 175, (1940). The reader must be referred to this article for discussions on the CO_2, H_2O, NH_3, CH_4 and the methyl halide molecules. A complete bibliography covering the period 1939-1942 on the Raman spectrum has been given by Glockler in the same journal, vol. 15, 111, (1943), and one covering the period previous to 1939 has been given by Hibben in the monograph "The Raman Effect and Its Chemical Applications" in 1939. As before, attention has been centered here on the interpretation of the spectra of the individual molecules. Molecules which are too complex to lend themselves to the normal coordinate treatments or for which the observed data are too meagre for a discussion of the normal vibrations, are not included.

Normal vibrations and valence force potential (II, §§1, 3B)*

Further developments of the mathematical method for the treatment of the normal vibrations of molecules have been given by Wilson.[1] With the aid of matrix algebra, vectors and the group theory, it is possible to find in a simple manner the kinetic energy of a molecule in terms of coordinates which are appropriate for potential functions of the valence force type, and to effect a reduction of the determinantal equation of a high order to those of lower orders in accordance with the symmetry of the molecule. Without troubling the nonmathematical readers with Wilson's method in its general form, we shall give explicitly the following slightly different but essentially equivalent treatment for the triangular YX_2 molecule with the valence field. It serves to illustrate sufficiently the reduction in labor in the solution of the problem of normal vibrations by the application of a little matrix algebra.

The kinetic energy T of the system YX_2 in rectangular coordinates is

$$2\,T = M(\dot{X}^2 + \dot{Y}^2) + m(\dot{x}_1^2 + \dot{y}_1^2 + \dot{x}_2^2 + \dot{y}_2^2) \tag{1}$$

and the potential energy for valence force field is, in the notation of P. 19,

$$2\,V = k(\delta r_1)^2 + k(\delta r_2)^2 + k_\alpha(r\delta\theta)^2. \tag{2}$$

---

[1] E. B. Wilson, Jr., Jour. Chem. Phys. 7, 1047 (1939); 9, 76 (1941). Application of this method to the C_2H_2, C_2H_6, CH_3CCCH_3, CH_3CCH, HCN, CH_3CN and the methyl halides has been made by Crawford and Brinkley, ibid. 9, 69 (1941).

*The Roman numerals and the §, etc., refer to the chapter, section and page in the present volume where the addendum is made.

On introducing the matrices for the rectangular and the internal coordinates

$$X \equiv (X\ Y\ x_1 y_1\ x_2 y_2), \qquad R \equiv (\delta r_1\ \delta r_2\ r\delta\theta) \tag{3}$$

and their transpose

$$\tilde{X} \equiv \begin{pmatrix} X \\ Y \\ x_1 \\ y_1 \\ x_2 \\ y_2 \end{pmatrix} \qquad \tilde{R} \equiv \begin{vmatrix} \delta r_1 \\ \delta r_2 \\ r\delta\theta \end{vmatrix} \tag{3'}$$

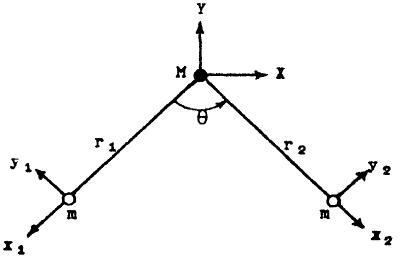
and the matrices

$$M \equiv \begin{pmatrix} M & & & & & \\ & M & & & 0 & \\ & & m & & & \\ & & & m & & \\ & 0 & & & m & \\ & & & & & m \end{pmatrix} \qquad K \equiv \begin{pmatrix} k & & 0 \\ & k & \\ 0 & & k_\alpha \end{pmatrix}, \tag{4}$$

T and V can be written, according to the rule of matrix multiplication, in the form

$$2\,T = XM\tilde{X}, \qquad 2\,V = RK\tilde{R}. \tag{5}$$

To find the relations between the rectangular coordinates and the internal coordinates, let us take the coordinate axes in directions as shown in the figure. Then, up to small quantities of the first order,



$$\begin{aligned} \delta r_1 &= s\,X + c\,Y + x_1 \\ \delta r_2 &= -s\,X + c\,Y + x_2 \\ r\delta\theta &= -2s\,Y + y_1 + y_2 \end{aligned} \tag{6}$$

where $c = \cos\frac{\theta}{2}$, $s = \sin\frac{\theta}{2}$. Now introduce the transformation matrix B and the transpose $\tilde{B}$

$$B \equiv \begin{pmatrix} s & c & 1 & 0 & 0 & 0 \\ -s & c & 0 & 0 & 1 & 0 \\ 0 & -2s & 0 & 1 & 0 & 1 \end{pmatrix} \qquad \tilde{B} \equiv \begin{pmatrix} s & -s & 0 \\ c & c & -2s \\ 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7}$$

Then (6) can be written

$$\tilde{R} = B\tilde{X}, \quad \text{or} \quad R = X\tilde{B} \tag{8}$$

and (3) becomes

$$2\,T = XM\tilde{X}, \qquad 2\,V = X\tilde{B}KB\tilde{X}. \tag{9}$$

The determinantal equation is hence

$$\| M\lambda - \tilde{B}KB \| = 0. \tag{10}$$

Let us now multiply this matrix equation from the right and from the left by the matrix

$$N \equiv \begin{pmatrix} M^{-\frac{1}{2}} & & & & & \\ & M^{-\frac{1}{2}} & & & 0 & \\ & & m^{-\frac{1}{2}} & & & \\ & 0 & & m^{-\frac{1}{2}} & & \\ & & & & m^{-\frac{1}{2}} & \\ & & & & & m^{-\frac{1}{2}} \end{pmatrix} \tag{11}$$

and denote by L the matrix

$$L \equiv \begin{pmatrix} k^{\frac{1}{2}} & & 0 \\ 0 & k^{\frac{1}{2}} & \\ & & k_\alpha^{\frac{1}{2}} \end{pmatrix} BN = \begin{pmatrix} s(\frac{k}{M})^{\frac{1}{2}} & c(\frac{k}{M})^{\frac{1}{2}} & (\frac{k}{m})^{\frac{1}{2}} & 0 & 0 & 0 \\ -s(\frac{k}{M})^{\frac{1}{2}} & c(\frac{k}{M})^{\frac{1}{2}} & 0 & 0 & (\frac{k_\alpha}{M})^{\frac{1}{2}} & 0 \\ 0 & -2s(\frac{k}{M})^{\frac{1}{2}} & 0 & (\frac{k_\alpha}{m})^{\frac{1}{2}} & 0 & (\frac{k_\alpha}{m})^{\frac{1}{2}} \end{pmatrix} \tag{12}$$

and the transpose

$$\tilde{L} \equiv N\tilde{B} \begin{pmatrix} k^{\frac{1}{2}} & & 0 \\ 0 & k^{\frac{1}{2}} & \\ & & k_\alpha^{\frac{1}{2}} \end{pmatrix}.$$

Then (10) becomes

$$\|\tilde{L}\,L - \lambda E\| = 0 \tag{13}$$

where E is the unit matrix of order 6 × 6. The roots λ's are the latent roots of $\tilde{L}\,L$, which, by a theorem in algebra, are those of L L and zeros. Hence

$$\|L\,\tilde{L} - \lambda E\| = 0 \tag{14}$$

where E is the unit matrix of order 3 × 3. The three zero roots of λ correspond to the two degrees of freedom of translation of the system of particles as a whole in its plane, and the one degree of freedom of rotation about an axis through the c.g. perpendicular to its plane. The three roots of (14) give the normal frequencies of the system YX_2.

To obtain the three roots of $L\tilde{L}$, let us transform (14) by a unitary transformation of matrix S, namely, $\tilde{S}S = S\tilde{S} = E$, such that

$$S = \begin{pmatrix} a & a & 0 \\ -a & a & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad a = (2)^{-\frac{1}{2}}$$

Then (14) becomes

$$\|SL\cdot\tilde{L}\tilde{S} - \lambda E\| = \begin{vmatrix} k(\frac{1}{m} + \frac{2}{M}c^2) - \lambda & 0 & -2\frac{(2kk_\alpha)^{\frac{1}{2}}}{M}cs \\ 0 & k(\frac{1}{m} + \frac{2}{M}s^2) - \lambda & 0 \\ -2\frac{(2kk_\alpha)^{\frac{1}{2}}}{M}cs & 0 & 2k_\alpha(\frac{1}{m} + \frac{2}{M}s^2) - \lambda \end{vmatrix} = 0 \tag{15}$$

which gives equations (22) on page 20.

In the above calculation, no use is made of the symmetry of the vibrations in effecting a factorization of the determinantal equation at the outset. This can be done as follows: For the symmetrical vibrations (with respect to the symmetry axis), we set $X = 0$, $x_1 = x_2$, $y_1 = y_2$, $\delta r_1 = \delta r_2$. Then

$$B = \begin{pmatrix} c & 1 & 0 \\ -2s & 0 & 1 \end{pmatrix}, \quad M = \begin{pmatrix} M & 0 & 0 \\ 0 & 2m & 0 \\ 0 & 0 & 2m \end{pmatrix}, \quad k = \begin{pmatrix} 2k & 0 \\ 0 & k_\alpha \end{pmatrix}, \text{ etc.}$$

The determinantal equation $\|\tilde{L}\,L - \lambda E\| = 0$ gives one zero root and two others given by $\|L\,\tilde{L} - \lambda E\| = 0$ which is readily shown to be the same as that obtained by removing the middle row and the middle column in (15). The zero root corresponds to the translation of the system along the directions of the symmetry axis.

For the antisymmetric vibration, we set $Y = 0$, $x_1 = -x_2$, $y_1 = -y_2$, so that $\delta r_1 = -\delta r_2$ and $r\delta\theta = 0$. Then

$$B = (s \quad 1 \quad 0), \quad M = \begin{pmatrix} M & 0 & 0 \\ 0 & 2m & 0 \\ 0 & 0 & 2m \end{pmatrix}, \quad k = (2k), \quad V = \begin{pmatrix} M^{-\frac{1}{2}} & 0 & 0 \\ 0 & (2m)^{-\frac{1}{2}} & 0 \\ 0 & 0 & (2m)^{-\frac{1}{2}} \end{pmatrix}$$

The equation gives two zero roots, corresponding to the translation of the system along directions perpendicular to the symmetry axis in its plane, and the rotation of the system about an axis perpendicular to its plane, and another root $\|L\,\tilde{L} - \lambda E\| = k(\frac{1}{m} + \frac{2}{M}s^2) - \lambda = 0$.

(III, §5, C, P. 90)

The statement that the effect of the coupling between the vibration and the rotation of a polyatomic molecule on the partition function and hence the thermodynamical properties is negligible is established by the calculation of Wilson, Jour. Chem. Phys. 7, 948, (1939).

(IV, §4, A, P. 135)

The general theory of the vibration-rotation energy of a polyatomic molecule has been given by H. H. Nielsen, Phys. Rev. 60, 794, (1941); 61, 540 (1942); Also Report on Progress in Physics, Vol. VII, 44, (1941).

CO_2 (V, §1, A, P. 144)

Dennison, Rev. Mod. Phys. 12, 175 (1940), has given a new evaluation of the potential function of the CO_2 molecule. The result is:

$$\begin{array}{llll}
\omega_1 = 1351.2 & x_{11} = -0.8 & x_{12} = 5.7 & x_{ll} = 1.7 \\
\omega_2 = 672.2 & x_{22} = -1.3 & x_{13} = -21.9 & \\
\omega_3 = 2396.4 & x_{33} = -12.5 & x_{23} = -11.0 & \\
a = -30 & d = 1.5 & g = 1.9 & \\
b = 71.3 & e = \begin{cases} 0.5 \\ -3.7 \end{cases} & h = 8.9 & \\
c = -250 & f = 6.4 & i = -25.7 &
\end{array}$$

HCN (V, §1, A, P. 150)

The weak Raman line at 2062 cm^{-1}, formerly ascribed to HNC, is ascribed to the isotopic molecule $HC^{13}N$ by Herzberg, Jour. Chem. Phys. 8, 847, (1940), on consideration of the calculated isotope shift of -32.9 cm^{-1} compared with the observed -32 cm^{-1}. The weak band observed by Williams for the aqueous solution has, however, too great a shift ($\sim$90 cm^{-1}) to be ascribed to $HC_{13}N$.

Azide ion N_3^- (V, §1, A, P. 150)

The infrared and the Raman spectra of the azide ion in crystals and solutions have been studied by a number of authors. The observed data are summarized in the following table.

		$\nu_2(\perp)$	$2\nu_2$	ν_1	ν_3	$\nu_2+\nu_3$	$\nu_1+\nu_3$	*Observer*
NaN_3(solid)	Ra	636(0)	1267(2)	1356(10)	2077(0)			Ven
NaN_3(sol'n)	Ra		1260(2)	1346(10)	2066(0)			Ven.; L
NaN_3(cryst)	Infra			-	-			Bal
αPb azide	Infra			-	2080	2702	3420	G
βPb azide	Infra			1352	2040	2702	3400	G

Infrared and Raman spectra of N_3^- ions

Ven. = Venkateswaran, Proc. Ind. Acad. Sc. A7, 144, (1938); L. = Langseth, Nielsen and Sørensen, Zeit. f. phys. Chem. B 27, 102, (1934); Bal = Bailey, quoted in Sutherland and Penney, Proc. Roy. Soc. A156, 678, (1936); G = Garner and Gomm, J. Chem. Soc. p. 2133, (1931)

The spectra of N_3^- have been discussed by Sutherland and Penney, loc. cit. It seems that the ion is linear. The appearance of $\nu_1 = 1352$ cm^{-1} in β lead azide and the band at 2702 cm^{-1}, whose probable interpretation is $\nu_2+\nu_3$, in the infrared indicate an asymmetrical structure for N_3^-, according to the selection rule on P. 70. This is also in accordance with the appearance of the $\nu_3 = 2070$ cm^{-1} in the Raman spectra. The weak Raman lines at $\sim$1260 cm^{-1} arise probably from a weak resonance between $2\nu_2(\perp)$ and ν_1.

H_2O, D_2O (V, §1, B, Pp. 159-65)

The pure rotational spectrum of D_2O in the region 26-139μ has been studied under high dispersion and resolution by Fuson, Randall and Dennison, Phys. Rev. 56, 982 (1939). Darling and Dennison, ibid., 57, 128, (1940), have carried through a second order perturbation calculation of the vibration-rotation energy of the H_2O molecule, in which resonance interactions between levels (v_1, v_2, v_3) and (v_1-2, v_2, v_3+2) are taken into account. A full discussion of the spectra of these molecules and their potential constants has been given by Dennison, Rev. Mod. Phys. 12, 175, (1940). The result is:

	H_2O	D_2O		H_2O	D_2O		H_2O	D_2O
ω_1 =	3825.3	2758.1	x_{11} =	-43.89	-22.81	x_{12} =	-20.02	-10.56
ω_2 =	1653.9	1210.3	x_{22} =	-19.50	-10.44	x_{13} =	-155.06	-81.92
ω_3 =	3935.6	2883.8	x_{33} =	-46.37	-24.37	x_{23} =	-19.81	-10.62

The potential constants in (29), P. 163, are, in 10^5 dynes/cm,

$k = 8.428$, $k_\alpha = 0.7678$, $k_1 = 0.1051$, $k_2 = 0.2521$

The rotational structure of the ν_1, ν_3, $\nu_1+\nu_3$, $\nu_2+\nu_3$ bands of H_2O has been further studied by H. H. Nielsen, Phys. Rev. 62, 422, (1942), and ν_2, $2\nu_2$ by Nielsen, ibid, 59, 565, (1941).

H_2Se, $HDSe$, D_2Se (V, §1, B, P. 109)

The infrared spectra of these molecules have been studied in greater detail by Cameron, Sears and Nielsen, Jour. Chem. Phys. 7, 994, (1939). The observed frequencies together with the constants in the potential (20), P. 19, that best fit the observed frequencies are given below.

	H_2Se	$HDSe$	D_2Se
ν_1	2260 D	1691 Z	1630 D
ν_2	1074 D	905 D	745 D
ν_3	2350 Z	2352 D	1696 Z

$k = 3.12 \times 10^5$, $k_\alpha = 0.32 \times 10^5$, H - H = 2.3 A, H - Se = 1.53 A

SO_2 (V, §1, B, P. 171)

The infrared bands of SO_2 have been studied under high dispersion. ν_2 = 1151.4 doublet type, rotational lines resolved; ν_2 = 517.8 doublet type, rotational lines resolved; ν_3 = 1361.5 zero branch type, unresolved. Cf. Barker, Rev. Mod. Phys. 14, 198, (1942)

NO_2 (V, §1, B, P. 172)

The ultraviolet absorption spectrum of NO_2 has been studied by Harris, King, Benedict and Pearse, Jour. Chem. Phys. 8, 705, (1940), who found 1319 cm^{-1} and 749 cm^{-1} for the normal electronic state. There seems to be no assignment of the observed infrared and the electronic bands which is satisfactory with respect to both the observed infrared band contours and the electronic bands. Further study of the infrared bands under higher dispersion and resolution is necessary.

New electron diffraction measurements by Maxwell and Moseley, ibid., 8, 738, (1940), give N - O = 1.21 ± 0.02 A and $\widehat{ONO}$ = 130° ± 2°.

C_2D , C_2HD (V, §2, A, Pp. 176-185)

The infrared spectra of these molecules have been studied under low dispersion by Stitt, Jour. Chem. Phys. 8, 56, (1940); and the 3340, 2560, 1202, 1340 cm^{-1} bands of C_2HD and the 2414, 1043 cm^{-1} bands of C_2D_2 have been studied by A. H. Nielsen, Phys. Rev. 57, 346, (1940). The observed bands and their assignments are given on the following page. A quantum mechanical treatment of the vibration-rotation energy of molecules of the C_2H_2 type has been given by Wu, Jour. Chem. Phys. 8, 489, (1940), and Shaffer and Nielsen, ibid., 9, 847, (1941).

C_2N_2 (V, §2, A, Pp. 186-7)

The Raman lines at 756 cm is not found by Reitz and Sabathy, Wien. Ber. 146, 577, (1938), and is hence probably spurious. This leaves the original assignment of the fundamental frequencies of Woo and Badger as the only probable one. The infrared spectrum has been further studied by Bailey and Carson, Jour. Chem. Phys. 7, 859, (1939). The observed bands and their assign-

C_2HD	Infra	Ra	C_2D_2	Infra	Ra
ν_1	1853 ∥	1851	ν_1		1762
ν_2	3340 ∥	3335	ν_2		2690
ν_3	2585 ∥		ν_3	2414	
ν_4	679 ⊥		ν_4	539 ⊥	
ν_5	519 ⊥		ν_5		
$\nu_4 + \nu_5$	1202 ∥		$\nu_4 + \nu_5$	1043 ∥	
$\nu_1 - \nu_5$	1330 ⊥		$\nu_1 - \nu_4$	1223 ⊥	
$2\nu_4$	1340 ∥				
$3\nu_4$	2043 ?		$3\nu_4$	1610 ⊥	
			$\nu_3 - \nu_5$	1927 ⊥	
			$\nu_2 - \nu_4$	2158 ⊥?	
			$\nu_1 + \nu_4$	2312	
			$\nu_3 + \nu_5$	2940	
$\nu_2 + \nu_4$	3950		$\nu_2 + \nu_4$	3280	
$2\nu_3$, $\nu_1 + \nu_2$	5110		$\nu_2 + \nu_3$	5120	

ments on the basis of the Woo-Badger fundamentals are as follows: $\nu_1 - \nu_4 = 618$⊥; $\nu_4 + \nu_5 = 732$∥; $2\nu_5 = 1026$ Raman; $\nu_2 - \nu_4 = 2093$⊥; $\nu_2 + \nu_4 = 2563$⊥; $\nu_3 + \nu_5 = 2663$⊥.

NH_3, ND_3 (V, §2, B, Pp. 192-199)

A full discussion of these molecules has been given by Dennison, Rev. Mod. Phys. 12, 175, (1940), who gives the following constants:

	NH_3	ND_3
ω_1 ∥	3539	2524
ω_2 ⊥	3622	2670
ω_3 ∥	1055	803.4
ω_4 ⊥	1685.4	1221.6
I_A	2.814×10^{-40}	5.447×10^{-40}
I_C	4.452×10^{-40}	8.898×10^{-40}
ξ_2	0.064	0.185
ξ_4	−0.270	−0.368

H - H = 1.631 A
N - H = 1.014 A
height of pyramid = 0.377 A

The potential constants in the potential (69), P. 189, evaluated with the zeroth-order frequencies ω's and the theory of Coriolis interactions are:

For ⊥ vibrations,	A = 10.494,	D = 1.366,	E = 2.41
For ∥ vibrations,	B = 3.171,	C = 2.270,	F = 1.78

in 10^5 dynes/cm. (Dennison's notations are: $\alpha = A$, $\beta = 3D$, $\gamma^2 = 3E^2$, $a = B$, $b = 3C$, $c^2 = 3F^2$).

Sheng, Barker and Dennison, Phys. Rev. 60, 786, (1941), further resolved the rotational "lines" of the ν_3(∥) fundamental into multiplets. This splitting results from the effect of the rotational distortion of the potential field determining the tunnel effect.

The splitting of the pure rotational lines into multiplets predicted by Slawsky and Dennison (see P. 328) has been observed by Foley and Randall, Phys. Rev. 59, 171, (1941), for J = 11, 12, 13, 14, 15. They obtain a value 1.3×10^{-18} c.g.s. for the dipole moment of the molecule.

Concerning the $\nu_2(\perp)$ fundamental, Sutherland's suggestion, Phys. Rev. 56, 836, (1939), that the two ⊥ bands 2441, 1473 cm^{-1} be interpreted as $\nu_3 + \nu_4$ meets with the difficulty that the separation $\Delta\nu$ should then be the same as that in ν_4, namely, 3.9 cm^{-1}, while the observed separations are ~16 cm^{-1}.

PH_3, PD_3, AsH_3, AsD_3, (V, §2, B, P. 200)

The Raman spectrum of PD_3 has been studied by de Hemptinne and Delfosse, Bull. Sc. Acad. Roy. Belg. 21, 793, (1935); that of AsH_3 and AsD_3 by Delfosse, Nature 137, 868, (1936). The infrared spectra of these molecules have been studied by Lee and Wu, Trans. Faraday Soc. 35, 1369, (1939); Sutherland, Lee and Wu, ibid., 35, 1373, (1939). The data are summarized below.

	PH_3		PD_3		AsH_3		AsD_3	
	Infra	Ra	Infra	Ra	Infra	Ra	Infra	Ra
$\nu_1 \parallel$	2327 ∥	2306	1694	1684 gas	2122 ∥	2094	1534	1508
$\nu_3 \parallel$	990 ∥	979	730	740 liq	906 ∥	910	660	630
$\nu_2 \perp$	2423				2185			
$\nu_4 \perp$	1121.5 ⊥	1115	806	807 liq	1005	990	714	730
?	992.4 ⊥							
$\nu_1 + \nu_4$	3428 ⊥				3091			
$\nu_1 + 2\nu_4$	4541							
$2\nu_1$					4160			
$2\nu_3$					6138 ∥			

PH_3: $I = 6.22 \times 10^{-40}$, $P - H = 1.46 A$, $H - P - H = 99^\circ$, ht. of pyramid = 0.67A
AsH_3: $I = 7.4 \times 10^{-40}$, $As - H = 1.56 A$, $H - As - H = 97^\circ$, ht. of pyramid = 0.75A

$AsBr_3$ (V, §2, B, P. 201)

The Raman spectrum has been studied by Braune and Engelbracht, Zeit. f. phys. Chem. B 19, 303, (1932), and Finkelstein and Kurnosova, Acta Physicochim. U.S.S.R. 4, 123, (1936).

	$\nu_1(\parallel)$	$\nu_2(\perp)$	$\nu_3(\parallel)$	$\nu_4(\perp)$
liq.	273(10)		128(6)	96(6)
gas	287			

OCH_2 (V, §2, D, P. 210)

From the value $I = 21.4 \times 10^{-40}$ obtained by Dieke and Kistiakowsky for OCH_2 and assuming the $C - H = 1.071$ A and $\widehat{HCH} = 119^\circ 55'$ obtained for C_2H_4 (see below), one obtains the value $O - C = 1.21$ A which differs considerably from the value 1.15A obtained by electron diffraction method and is much more in line with the low value for the $C = O$ bond constant $k = 12.06 \times 10^5$ (compared with the bond constant 15.9×10^5 and $C - O = 1.15$ A for CO_2).

A normal coordinate treatment employing the most general potential consistent with the symmetry C_{2v} for the OCH_2 type molecules has been given by Silver and Ebers, Jour. Chem. Phys. 10, 559, (1942).

Coriolis perturbations in OCD_2 is studied by Nielsen, Phys. Rev. 55, 289, (1939).

OSF_2, $OSCl_2$ (V, §2, E, Pp. 213-4)

In view of the polarization data for $OSCl_2$ of Cabannes and Rousset, Ann de Physique 19, 229, (1933), and Venkateswarlu, Proc. Ind. Acad. Sc. A 10, 156, (1939), the assignment given on P. 214 should probably be changed as follows:

	$\nu(S\text{-}O)$	$\nu_3(SCl_2)$	$\delta(SCl_2)$	$\delta(OSCl_2)$	$\nu_1(SCl_2)$	$\delta(O\text{-}S\text{-}Cl_2)$
$OSCl_2$	1229 m	443 s	343 vs	282 s	488 s	192 s
ρ	0.13	6/7	0.15	6/7	0.08	0.45(C.R.); 0.78(V.)

H_2O_2, D_2O_2 hydrogen peroxide (V, §2, F, P. 214)

The Raman spectra of these molecules have been studied by Simon and Feher, Zeit. f. Elektrochem. 41, 290, (1935), and Feher, ibid., 43, 663, (1937). H_2O_2: 877, 1420, 3400 cm^{-1}; D_2O_2: 1009, 2510 cm^{-1}. From the study of two bands at 10,291.08 and 10,283.68 cm^{-1} in the photographic infrared, Zumwalt and Giguere, Jour. Chem. Phys. 9, 458, (1941), found Q branches characteristic of both the $\|$ and the $\perp$ bands of a symmetrical rotator. This hybrid character rules out the cis planar structure of the two O-H bonds, since this structure would show either pure $\|$ or pure $\perp$ bands. The observed large electric moment of H_2O_2 precludes the trans configuration since this would have zero electric moment. Hence these authors suggest a nonplanar structure, in agreement with the theoretical result of Penney and Sutherland, Jour. Chem. Phys. 2, 492, (1934), and the X-ray study of the $CO(NH_2).H_2O_2$ crystal by Lu, Hughes and Giguere, J. Am. Chem. Soc. 63, 1507, (1941), indicating, respectively, an azimuthal angle of $\sim 100^\circ$ and 105°. The presence of two bands displaced by 7.4 cm^{-1} from each other is suggested to be due to the splitting of the vibrational levels by the tunnel effect for the two-minima in the potential of relative orientation of the two O-H bonds.

On accepting this nonplanar structure, the H_2O_2 belongs to the point group C_2, and there should be 4 symmetric (with respect to the axis) and two antisymmetric vibrations. The nature of the 4 symmetric vibrations would be roughly as follows: one is the symmetric O-H valence vibration, one is the O-O vibration, one the O-O-H bending and one the torsional oscillation of the O-H bonds about the O-O axis. The Raman lines

3400 (H_2O_2),	877 (H_2O_2),	1420 (H_2O_2)
2510 (D_2O_2)		1009 (D_2O_2)

may be immediately ascribed to the first 3 of these vibrations. The two antisymmetric vibrations are the O-H valence and O-O-H bending vibrations. They are inactive in Raman effect and have actually not been observed. Only the torsional vibration is missing in the Raman spectrum.

HN_3 hydrazoic acid (V, §2, G, P. 214)

The Raman spectrum has been studied by Engler and Kohlrausch, Zeit. f. phys. Chem. B 34, 214, (1936), and the infrared spectrum by Davis, Trans. Faraday Soc. 35, 1184, (1939), and Eyster and Gillette, Jour. Chem. Phys. 8, 369, (1940). There should be 6 fundamentals for a structure in which the 3 N atoms are linear (see azide ion N_3^- above) and the H atom is attached to an N atom at one end off the line of the N atoms. The observed data and their interpretation are as follows:

ν_1	ν_{NH}	3335.6	Inf.		$\nu_3 - \nu_5$, $\nu_4 - \nu_6$	526	Inf.
ν_2	ν_{NN}	2140.4	"		$\nu_5 + \nu_6$	1381	"
ν_3	ν'_{NN}	1269.0	"	1300 Ra.	$2\nu_4$	2303	"
ν_4	δ_{HNN}	1152.5	"		$2\nu_1 + 2\nu_4$	8802	"
ν_5	δ_{NNN}	738.8	"		$3\nu_1$	9547	"
ν_6	δ'_{NNN}	657.9	"		$3\nu_1 + \nu_4$	10690	"
	?			2389 Ra.	$4\nu_1$	12412	"

The bands $3\nu_1$ and $4\nu_1$ have been studied in the photographic infrared by Herzberg, Patat and Verleger, Zeits. Elektrochem. 41, 522, (1935); Verleger, Phys. Zeits. 38, 83, (1937).

Methane and deuteromethane (V, §3, B, Pp. 217-229)

The spectra, the potential function and the Coriolis perturbations of these molecules have been fully discussed by Dennison, Rev. Mod. Phys. 12, 175, (1940). The zeroth-order frequencies are estimated by a reasonable procedure.

CH_4	ω_1 = 3029.8	ω_2 = 1390.2	ω_3 = 3156.9	ω_4 = 1357.6
CD_4	ω_1 = 2143.2	ω_2 = 983.4	ω_3 = 2336.9	ω_4 = 1026.4

The potential constants given in (126), P. 225, have been reevaluated from these ω's. They are, in 10^5 dynes/cm,

$$A = 8.568, \quad B = 0.5186, \quad C = 0.3048, \quad D = 1.4216, \quad E = 0.3406.$$

From these, the constants in the potential (111), P. 219, containing central and valence forces can be calculated from (114), P. 220. They are, in 10^5 dynes/cm,

$$k_{CH} = 5.835, \quad k_\alpha = 0.498, \quad k_{HH} = -0.101, \quad k_2 = 0.176.$$

The criterion (113a), namely, $D = 10B - 2C - 8E$, for the potential (111) to hold is not satisfied exactly. The introduction of an interaction term such as $k_3\ \Sigma(\delta r_i)(r\delta\alpha_{ij})$ in the potential (111) may be useful.

SiH_4, GeH_4 (V, §3, B, Pp. 229-231)

In footnote 2, P. 231, the unsatisfactory nature of the molecular dimension obtained for GeH_4 was pointed out and ascribed to the uncertainty in the observed value of $\Delta\nu_4$. Murphy, Jour. Chem. Phys. 8, 71, (1940), finds from a calculation of the Coriolis perturbations that the observed and the theoretical structure of the ν_4 bands do not agree. It is pointed out by Wu, ibid., 9, 195, (1941), that this may be due to the use of the incorrect value 7×10^{-40} for the moment of inertia of GeH_4. Assuming pure valence force potential, Wu obtained, from the theory of Jahn, Proc. Roy. Soc. A 168, 469, (1938), $\zeta_3 = 0.018$, and $I = 9.78 \times 10^{-40}$ for GeH_4. The problem is finally satisfactorily settled by a complete analysis of the spectra of SiH_4 and GeH_4 by Tindal, Straley and Nielsen, Proc. Nat. Acad. Sc. 27, 208, (1941); Phys. Rev. 62, 151, (1942); 62, 161, (1942). The result is summarized below.

	ν_2	$\Delta\nu_2$	ν_3	$\Delta\nu_3$	ν_4	$\Delta\nu_4$	*I from* ν_3, ν_4	*I from* ν_2	*X - H*
SiH_4	975	5.62	2191	5.64	910	2.77	9.98×10^{-40}	9.98×10^{-40}	1.50A
GeH_4	9.32	5.275	2114	5.67	818	2.27	10.57×10^{-40}	10.61×10^{-40}	1.54A

$GeCl_4$ (V, §3, B, P. 233)

The Raman spectrum has been studied by Haun and Harkins, J. Am. Chem. Soc. 54, 3917, (1932). The observed frequencies are:

ν_1 = 397, ν_2 = 132, ν_3 = 451, ν_4 = 171.

Methyl halides (V, §3, C, Pp. 235-242)

The Raman line 1098 cm^{-1} of CH_3Cl (see Table IL) is found to be polarized and hence its identification with the degenerate vibration $\nu_6(\perp)$ is not satisfactory.

From the 1355 cm^{-1} band of CH_3Cl, Nielsen and Nielsen obtained the distance C - Cl = 1.53A, differing greatly from the value 1.66A given by Sutherland (see footnotes 7 and 6, P. 239). It was pointed out, however, by Sutherland, Jour. Chem. Phys. 7, 1066, (1939), that an alternate numbering of the rotational lines of CH_3Cl^{35} and CH_3Cl^{37} in the work of the Nielsens leads to $\Delta\nu \simeq 0.95 - 1.0$ cm^{-1}. This gives $I_A \simeq 56 - 59 \times 10^{-40}$ and C - Cl $\simeq$ 1.66 - 1.71A.

Lagemann and Nielsen, Jour. Chem. Phys. 10, 668, (1942), have reexamined under improved conditions all the fundamentals except ν_6 = 532 cm^{-1} of CH_3I in the infrared.

Potential functions of the modified valence force type for the methyl halides have been calculated by Slawsky and Dennison, Jour. Chem. Phys. 7, 522, (1939), Linnett, ibid., 8, 91, (1940); and Crawford and Brinkley, ibid., 9, 69, (1941). See last section of this Supplement and the last table.

CD_3Cl, CD_3Br.

The infrared spectra of these molecules have been studied by Noether, Jour. Chem. Phys. 10, 664, (1942), in the region 2.8 - 18μ. All the fundamental frequencies are identified.

Table LIII, P. 243.

To the molecules in Table LIII, the following may be added. The assignment of the observed Raman frequencies in each case is guided, in the absence of polarization data, by considerations of the trend in the frequencies in passing from one to another of these molecules. (See Table at top of next page.)

Halogen derivatives of methane (V, §3, D, Pp. 244-254)

Wu, Jour. Chem. Phys. 10, 116, (1942), has discussed fully the assignment of the fundamental frequencies of all the halogen derivatives of methane and the connections between the frequencies in passing from CH_4 to CX_4 through the series CH_4 - CH_3X - CH_2XY - CH_2X_2 - CHX_2Y - CHX_3 - CX_4. Complete references to the experimental data are given there.

	$\nu_1 \parallel$	$\nu_2 \perp$	$\nu_3 \parallel$	$\nu_4 \perp$	$\nu_5 \parallel$	$\nu_6 \perp$	*Observer*
CHF_3	1116.5(8)	936.8(0)	696.7(6)	508.1(5)	3062.0(10)	1376.2(3)	G. E.
$SiDCl_3$	489	555	252	129	1647	?	D.
$SiHBr_3$	362	470	166	115	2236	?	D. Gh., H
$SiDBr_3$	360	468	167	114	1616	?	D.
$SPCl_3$	432	543	246	171	750	312	T.; S. S.

G. E. = Glockler and Edgell, Jour. Chem. Phys. 9, 224, (1941), D. = Delfosse, Nature 137, 868, (1936); T. = Thatte, Nature 138, 468, (1936), H. = de Hemptinne and Delfosse, Ann. Soc. Sc. Bruxelles 36 B, 373, (1936), D. Gh. = Delfosse and Ghoovaerts, Bull. Sc. Acad. Roy. Belgium 21, 410, (1935), S.S. = Simon and Schulze, Naturwiss. 25, 669, (1937).

Edgell, Thesis, Iowa, (1941), (quoted in Glockler, Rev. Mod. Phys. 15, 111, (1943), differs from Wu, loc. cit., only in interchanging the assignments of $A_2:\delta = 898$ cm^{-1}, B: $\delta_1(a) = 1149$ cm^{-1} in CH_2Cl_2 so that A_2: $\delta = 1149$ cm^{-1}, B: $\delta_1(a) = 898$ cm^{-1}. Both assignments have the same difficulty that while the $A_2:\delta$ vibration should be inactive in the infrared, both the 898 and the 1149 cm^{-1} are observed in the infrared by Corin and Sutherland, Proc. Roy. Soc. A165, 43, (1938). A definite choice between these two assignments probably cannot be made on the basis of the data now available. The correctness of the sets of fundamental frequencies of CH_2BR_2, CH_2Cl_2, and of the other halogen methanes, can, however, not be doubted in view of the good agreement between observed and the calculated specific heats of these molecules, as shown by Edgell and Glockler, Jour. Chem. Phys. 9, 484, (1941).

A normal coordinate treatment of the CH_2X_2 molecules has been given by Wagner, Zeit. f. phys. Chem. B 45, 69, (1939); Wu, loc. cit.; and Edgell, loc. cit.

HCOOH, HCOOD, DCOOH, DCOOD, $(DCOOH)_2$, $(DCOOD)_2$ (V, §3, F, P. 255)

The infrared spectra of these acids have been studied under low dispersion by Herman and Williams, Jour. Chem. Phys. 8, 447, (1940).

C_2H_4, C_2D_4 (V, §4, B, Pp. 265–271)

The infrared spectra of these molecules have been studied under high dispersion by Barker and Gallaway, Jour. Chem. Soc. 10, 88, (1942). The following table summarizes the fundamentals together with a plausible assignment of the combination bands in C_2D_4.

In the table, the torsional frequency $\delta = 825$ for C_2H_4 is, as on P. 267, calculated from the Raman frequency $1656 = 2\delta$. The value 585 for C_2D_4 is then calculated from this by means of the relation $(\delta)_H/(\delta)_D = (m_D/m_H)^{\frac{1}{2}}$. The value $\delta_{\sigma' s} = 1055$ for C_2H_4 is calculated from the newly observed band $\delta_{\sigma' a} = 995$ together with the interpretation of the band 2047 cm^{-1} as $\delta_{\sigma' s} + \delta_{\sigma' a}$. The values $\delta_{\sigma' s} = 850$ and $\delta_{\sigma' a} = 750$ for C_2D_4 are calculated by means of the relation (106f) on P. 264 together with the interpretation that the infrared band 1595 cm^{-1} is $\delta_{\sigma' s} + \delta_{\sigma' a}$.

Concerning the fundamentals in these ethylenes, the following can be said. There can be no doubt as to the correctness of the A_{1g}, A_{2u}, B_{1u} and B_{2u} frequencies. The B_{1g} frequency, although not yet observed in the Raman spectrum, can also be regarded as fairly certain. The A_{1u} torsion frequency $\delta = 825$ cm^{-1} for C_2H_4 is most probably correct in view of the specific heat

		C_2H_4		C_2D_4		C_2D_4		
						Infra.		
		Infra.	Ra.	Infra.	Ra.	μ	cm^{-1}	Assignment
A_{1s}	$\nu_{\pi s}$		3019.3		2251.8	10.88	919	?
	$\nu_{2\pi s}$		1623.3		1514.5	7.76	1290	?
	$\delta_{\pi s}$		1342.4		981.3	6.27	1595	$\delta_{\sigma' s} + \delta_{\sigma' a}$
A_{2a}	$\nu_{\pi a}$	2989.5		2200.2		3.28	3050	$\delta_{\sigma s} + \nu_{\sigma a}$; $\delta_{\sigma a} + \nu_{\sigma s}$
	$\delta_{\pi a}$	1443.9		1077.9		3.12	3200	$\delta_{\pi s} + \nu_{\pi a}$
B_{2s}	$\nu_{\sigma s}$		3069 ?		2306	2.98	3350	$\nu_{\pi s} + \delta_{\pi a}$; $\nu_{\sigma a} + \delta_{\pi s}$
	$\delta_{\sigma s}$		944 ?		780	2.95	3390	$\nu_{\sigma s} + \delta_{\pi a}$
B_{1a}	$\nu_{\sigma a}$	3105.5		2345		2.59	3860	$\nu_{2\pi s} + \nu_{\sigma a}$
	$\delta_{\sigma a}$	950		720		2.26	4425	$\nu_{\pi s} + \nu_{\pi a}$
B_{1s}	$\delta_{\sigma' s}$		(1055)		(850)	2.23	4480	$\nu_{\sigma s} + \nu_{\pi a}$
B_{2a}	$\delta_{\sigma' a}$	995		(750)		2.16	4625	$\nu_{\sigma s} + \nu_{\sigma a}$
A_{1a}	δ	(825)		(585)				

C - C = 1.353A, C - H = 1.071A, $\widehat{HCH}$ = 119°55'

data of Burcik and Eyster, Jour. Chem. Phys. 9, 118, (1941). One is then left with the two vibrations $\nu_{\sigma s}$, $\delta_{\sigma s}$ in the class B_{2s}. For C_2D_4, they are probably given by the Raman lines 2306 and 780 cm^{-1}. For C_2H_4, one may assign the Raman line at ~944 cm^{-1} to $\delta_{\sigma s}$ and that at 3069 cm^{-1} to $\nu_{\sigma s}$. There seems to be nothing implausible in these assignments of the B_{2s} frequencies, except for following consideration based on a normal coordinate treatment.

On the basis of the above assignments, it should be possible to calculate the constants in either the potential (158), P. 263, or the potential (161), P. 264, by means of the equations (160a) - (160d) or (162a) - (162d). It is found that equations (160c) for the B_{2s} vibrations give entirely inconsistent values for the potential constants compared with those obtained from the A_{1s}, A_{2a}, B_{1a} frequencies. Similar situation obtains when equations (162) are employed for the potential (161). One may blame the difficulty on the inadequacy of the potentials (158) and (161); but if this is the case, a drastic change, not the further inclusion of small interaction terms, is necessary to remove the above-mentioned inconsistency.

To obtain the potential function, from the A_{2a} and B_{1a} frequencies, we have, from either (160b), (160d) or (162b), (162d),

$$k + k_2 = 5.04, \quad H + \theta - \lambda \quad \text{or} \quad k_\alpha = 1.096 \quad \text{in } 10^5 \text{ dynes/cm}$$

$$k - k_2 = 5.02, \quad H - \theta + \lambda \quad \text{or} \quad k_\varphi = 0.511$$

As either (160a) or (162a) are then left with two unknown constants among three equations, we shall introduce the term k_3 in (161) into the potential (158) so that equations (160a) become

$$\lambda_1 + \lambda_2 + \lambda_3 = \frac{2}{M} k_1 + Q(k + k_2) + N(H + \theta + \lambda) + W k_3$$

$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_3\lambda_1 = \frac{2}{mM}[k_1(k+k_2) + \left\{k_1+\tfrac{1}{2}MG(k+k_2)\right\}(H+\theta+\lambda)+\tfrac{1}{2}W(k+k_2)k_3 - k_3^2]$$
$$= \frac{2}{m^2M}(k+k_2)[k_1(H+\theta+\lambda)-k_3^2].$$

With the above value for $k + k_2$, these equations are consistent with the following approximate values

$$k_1 = 9.87, \qquad H+\theta+\lambda = 1.06, \qquad k_3 = -0.22 \text{ in } 10^5 \text{ dynes/cm.}$$

As mentioned before, these values of the constants are not consistent with (160c) or (162c) for the vibrations $\nu_{\sigma s}$ and $\delta_{\sigma s}$. To show this, let us calculate the frequencies $\nu_{\sigma s}$ and $\delta_{\sigma s}$ from (160c), using the above potential constants. We find, for C_2H_4,

$$\nu_{\sigma s} = 3116 \text{ cm}^{-1}, \qquad \delta_{\sigma s} = 1225 \text{ cm}^{-1},$$

differing greatly from the values 3069 and 944 discussed before.

C_2Cl_4 (V, §4, B, P. 271)

Duchesne and Parodi, Nature 144, 382, (1939), report two infrared absorption bands at 332 and 387 cm^{-1}.

The weak Raman line at 383 cm^{-1} is shown by Wittek, Zeit. f. phys. Chem. B 48, 1, (1940), to be spurious.

Still no complete assignment of all the fundamentals is possible.

H_3CCN, H_3CNC (V, §4, D, Pp. 281-2)

The infrared spectrum of CH_3CN has been studied under low dispersion by Bell, J. Am. Chem. Soc. 57, 1023, (1936), and Gordy and Williams, Jour. Chem. Phys. 3, 664, (1935); 4, 85, (1936). The observed frequencies are $\nu_3 = 917$, $\nu_4 = 2283$, $\nu_5 = 3077$, $\nu_6 = 1412$, $\nu_7 = 1040$, in the notation of (172), P. 281. Electron diffraction measurements by Pauling, Springall and Palmer, J. Am. Chem. Soc. 61, 927 (1939), give the following distances

$$C - C = 1.49 \pm 0.03 \text{ A}, \qquad C - N = 1.16 \pm 0.03 \text{ A}.$$

The infrared spectrum of CH_3NC has been studied by Gordy and Williams, loc. cit. $\nu_4 = 2183$, $\nu_5 = 3077$ cm^{-1}. Brockway, J. Am. Chem. Soc. 58, 2516, (1936), gives the following distances

$$C - N = 1.48 \pm 0.03 \text{ A}, \qquad N - C = 1.17 \pm 0.03 \text{ A}.$$

The constants in a potential differing slightly from (170), P. 281, have been calculated for these two molecules by Linnett, Jour. Chem. Phys. 8, 91, (1940). See table at the end of this Supplement.

CH_3OH (V, §4, E, Pp. 282-5)

The problem of the hindered rotation of the O-H bond about the C - O axis has been treated quantum mechanically by Koehler and Dennison, Phys. Rev. 57, 1006, (1940). Comparison between the theory and the observations of Borden and Barker, Jour. Chem. Phys. 6, 553, (1938), and of Lawson and Randall (quoted by Koehler and Dennison) seems to indicate a potential barrier of the order 470 ± 40 cm^{-1} (~1400 cal/mole) for this hindered rotation. This value does not, however, agree with value ~3400 cal-mol. indicated by the observed entropy according to Russell, Osborne and Yost, J. Am. Chem. Soc. 64, 165, (1942).

CH_3SH methyl mercaptan (V, §4, E, P. 285)

The structure of this molecule is expected to be similar to that of methyl alcohol. The normal vibrations may be roughly described as follows. Considering first the CH_3-S as a methyl-halide-like symmetrical rotator, we have the vibrations $\nu_1(\|)$, $\nu_2(\perp)$, $\nu_3(\|)$, $\nu_4(\perp)$ characteristic of the CH_3 group and the $\nu_5(\|)$ and $\nu_6(\perp)$ characteristic of the C - S valence and the S - CH_3 bending vibrations. On taking the asymmetry due to the S - H bond into account, we expect the ⊥ vibrations to split into doublets. These then account for 9 normal vibrations. Of the remaining 3, ν_7 is roughly a S - H valence, ν_9 a C - S - H bending vibration, and ν_8 a torsional vibration or hindered rotation of the S - H bond about the C - S axis.

The Raman spectrum has been studied by Venkateswaran, Indian J. Phys. 5, 219, (1930); Phil. Mag. 15, 263, (1933); and by Wagner, Zeits. f. phys. Chem. B 40, 36, (1938). The infrared spectrum is studied and a discussion of the assignment of the fundamental frequencies is given by Thompson and Skerrett, Trans. Faraday Soc. 36, 812, (1940). The frequencies are given in the following table. On the basis of these frequencies, Russell, Osborne and Yost, J. Am. Chem. Soc. 64, 165, (1942), from measurements of the entropy, finds a potential barrier of ~1460 cal/mol. (~500 cm^{-1}) for the hindered rotation.

Notation	Nature of vibration	Observed Ra.	Infra.
ν_1	$\nu_{\|}(CH_3)$	2870(m)	~2870
ν_{2-1}	$\nu_{\perp}(CH_3)$	2932(s)	~3000
ν_{2-2}		2999(m)	~3000
ν_3	$\delta_{\|}(CH_3)$	1319(v.w.)	1335 ‖
ν_{4-1}	$\delta_{\perp}(CH_3)$	1438(w)	1475
ν_{4-2}			1430
ν_5	ν(C-S)	704(s)	704 ‖
ν_{6-1}	δ(CH -S)	1055(w)	1060 ⊥
ν_{6-2}			957 ⊥
ν_7	ν(S-H)	2573(s)	2597
ν_9	δ(C-S-H)	803(w)	803 ‖

CH_3CCH methyl acetylene (V, §5, C, Pp. 290-2)

The infrared and the Raman spectra, the former under low dispersion, have been studied by Crawford, Jour. Chem. Phys. 8, 526, (1940). The Raman spectrum shows an additional weak line at 1035 cm^{-1} which is believed to be the missing degenerate fundamental δ_0'' in Table LXXVIII. The infrared frequencies are $\nu_1 = 3430$, $\nu_3 = 2151$, $\nu_5 = 926\|$, $\nu_6 = 2995$, $\nu_8 = 642$, $\nu_{10} = 1040$. ν_2 at ~2900 cm^{-1} is masked by ν_6. ν_4 and ν_7 at 1380 - 1450 cm^{-1} overlap each other and are not resolved. A number of weak bands between 2.5 and 15μ can be satisfactorily explained on the basis of the fundamentals above and in Table LXXVIII.

Crawford, loc. cit., calculates the frequencies of CH_3CCH by means of a potential of the valence force type containing interaction terms and involving 13 constants which are carried over from those in C_2H_2, C_2H_6, CH_3CCCH_3. The agreement between the observed and the calculated frequencies is good in general. For the potential constants, see the table at the end of this Supplement.

$(CH_2)_2S$ ethylene sulfide (V, §5, D, P. 295)

The infrared and the Raman spectrum have been studied by Thompson and Dupre, Trans. Faraday Soc. 36, 812, (1940). The observed frequencies and their assignments are given in the following table. For notation, see Tables LXXIX and LXXX, Pp. 293-4.

Assignment		Raman	Infrared
A_1	ν_1	2990p	(2990)
	ν_2	1450p? w	1441
	ν_3	1120p	?
	ν_4	1040p	1042
	ν_5	625p	625
B_1	ν_6	2990	(2990)
	ν_7	?	1390
	ν_8	491vw	949
	ν_9	?	711
B_2	ν_{10}	3080m	(3080)
	ν_{11}	827w	823
	ν_{12}	?	686
A_2	ν_{13}	3080	-
	ν_{14}	?	-
	ν_{15}	660w	-

A number of bands between 2 and 10μ can be assigned as follows: $2\nu_5 = 1235$ w, $\nu_5 + \nu_{12} = 1316$, $\nu_4 + \nu_5 = 1724$ vw, $\nu_2 + \nu_5 = 2062$ m, $\nu_2 + \nu_{11} = 2270$ vw, $\nu_1 + \nu_{12} = 3676$ m, ? = 4250 vw, $\nu_2 + \nu_{10} = 4505$ m, $2\nu_1$; $\nu_1 + \nu_6$; $\nu_1 + \nu_{10} = 5988$ m.

CH_3NH_2 methylamine (V, §5, E, P. 295)

The Raman spectrum of CH_3NH_2 in solution has been recently studied by Edsall, Jour. Chem. Phys. 5, 225, (1937); and that of the gas by Kirby-Smith and Bonner; ibid., 7, 880, (1939). The infrared spectrum has been studied by Cleaves and Plyler, ibid., 7, 563, (1939); and under somewhat greater dispersion by Owens and Barker, ibid., 8, 229, (1940).

The structure of this molecule is similar to that of CH_3OH, except that now the O - H is replaced by NH_2. The normal vibrations may be roughly described as follows. Ignoring the two H atoms of the amine NH_2 group first, we have the symmetrical top CH_3-N and hence $\nu_1(\parallel)$, $\nu_2(\perp)$, $\nu_3(\parallel)$, $\nu_4(\perp)$ characteristic of the CH_3 group, and $\nu_5(\parallel)$ $\nu_6(\perp)$ characteristic of the C - N valence and N-CH_3 bending vibrations. When the asymmetry due to the H atoms in NH_2 is taken into account, each of the ⊥ vibrations above will split into two. These account then for 9 normal vibrations. There are then the 3 vibrations characteristic of the NH_2 group, one ν_{10} representing the bending of

C-N-H, and one ν_{11} the twisting of NH about the bisector of the angle $\widehat{HNH}$. The last degree of freedom is that of torsional oscillation or hindered rotation of the NH_2 about the C-N axis. The following table gives the observed frequencies and their plausible assignments.

Notation	Nature of vibration	Raman	Infrared	
			Ow. Bar.	Cl. Ply.
ν_1	$\nu_{\parallel}(CH_3)$	2820(8)	2820 Q	2819 Q
		2883(3)	2930 $\perp$	
ν_{2-1}	$\nu_{\perp}(CH_3)$	2900(6)p		2895 Q
ν_{2-2}		2960(10)	2964 Q	2968
ν_3	$\delta_{\parallel}(CH_3)$	sol. 1428(½b)	1385 Q	1426 Q?
ν_{4-1}	$\delta_{\perp}(CH_3)$	1460(6)	1470 $\perp$	1460 $\perp$
ν_{4-2}		?	?	?
ν_5	$\nu_{\parallel}(C-N)$	1047(7)p	1045.3 Q	1045 Q
ν_{6-1}	$\delta_{\perp}(C-CH_3)$	sol. 1110(0)	1130 ?	1127 Q
ν_{6-2}		sol. 1174(½b)	1150 ?	
ν_7	$\nu_{\parallel}(NH_2)$	3360(6)p	3360 Q	3360 Q
ν_8	$\nu_{\perp}(NH_2)$	3470(2)	3410 $\perp$	3425
ν_9	$\delta_{\parallel}(NH_2)$	sol. 1614(2b)	1625	1625 Q
ν_{10}	$\delta_{\parallel}(C-N-H_2)$	781(1)	763 Q 795 Q	783 Q
ν_{11}	$\delta_{\perp}(NH_2$ twisting)		620 Q?	
ν_{12}	torsion			

The presence of 4 frequencies near 2900 cm^{-1} may be due either to resonance interactions between the harmonics of the frequencies at 1430 or to the splitting of the ν_2, or both. Q denotes the Q branch which is characteristic of vibrations with electric moment parallel to the axis of a symmetrical rotator. As CH_3NH_2 is not exactly a symmetrical rotator, many vibrations will have both $\parallel$ and $\perp$ components (to the C-N axis) for the electric moment. The $\parallel$ and $\perp$ in the table only mean the predominent components.

From the measurements of the entropy, Aston and Doty, Jour. Chem. Phys. 8, 743, (1940), finds a potential barrier of ~1500 cal/mol. (520 cm^{-1}) for the hindered rotation of the NH_2 group about the C-N axis.

C_2H_6 (V, §6, A, Pp. 295-305)

The E_u ν_8 fundamental at 827 cm^{-1} in the infrared has been further studied by Owens and Barker, Jour. Chem. Phys. 10, 146, (1942).

The question whether the normal configuration of C_2H_6 has the staggered D_{3d} or the eclipsed D_{3h} form is in very much the same state as in 1939. All that can be said is that electron diffraction studies of 1,2 dichloroethane, dibromoethane, chlorobromoethane indicate the trans and hence the staggered structure (footnote 8, P. 311), and electron diffraction measurements on symmetrical tetrachloroethane definitely indicate the trans and the C_2 staggered structure (Shoemaker and Stevenson, Jour. Chem. Phys. 8, 639, (1940)). In no case is there evidence for the eclipsed structure, and the general belief is that the D_{3d} form is the more stable one for ethane also.

B_2H_6 (V, §6, A, Pp. 305-6)

The infrared and the Raman spectra have been studied by Stitt, Jour. Chem. Phys. 9, 780, (1941). The paper is unfortunately unavailable to the writer.

Al_2Br_6 (V, §6, A, P. 306)

The Raman spectrum has been studied by Rosenbaum, Jour. Chem. Phys. 8, 643, (1940), who observed the following frequencies: ν_1 = 67(5) ν_2 = 79.3(5), ν_3 = 1128(5), ν_4 = 140.3(5), ν_5 = 208.2(10), $\nu_1 + \nu_3$ = 185(0), $\nu_2 + \nu_4$, $2\nu_3$ = 223(1), $2\nu_5$ = 407(0), $2\nu_5 + \nu_2$ = 488(1d). No discussion of the assignment of these frequencies can be definite on the basis of these data alone.

1,2 dihalogen ethanes (V, §6, B, Pp. 306-312)

Additional Raman frequencies for $C_2H_4I_2$ have been given by Kahovec and Kohlrausch, Ber. 73B, 159, (1940); also Kohlrausch and Wittek, Zeit. f. phys. Chem. B 47, 55, (1940). The assignment of the observed frequencies in accordance with the tables on Pp. 309-10 is as follows:

trans	A (Ra.)	925(½)	582(0)	2953(4)	1208(4)	1038(3)	131(5)
	B (In.)		635	3000	1400	1040	?
	B'(Ra.)			2999(½)	1417(4)	?	
	A'(In.)			3000	1128	720	
cis	A_1(Ra.)	842(3)	440(3)	2952(4)	?	?	?
	(In.)	840		3000			
	B_1(Ra.)	512(0)	512(0)	?	?	?	?
	(In.)			3000	1400		
	B_2(In.)			3000		778	
	A_2(Ra.)			?	?	1158(1)	?

The Raman spectrum of $C_2D_4Br_2$ has been studied by Mizushima, Morino and Sugiura, Proc. Imp. Acad. Tokyo 14, 250, (1938); Proc. Ind. Acad. Sc. A, Raman Jubilee Vol., 315, (1938). The following data are taken from Kolrausch and Wittek, loc. cit. The assignment of the frequencies in accordance with the tables on Pp. 309-310 is as follows:

trans	A (Ra.)	907(3)	607(10)	2188(5)	992(10)	?	188(10)
	B'(Ra.)			2263(3)	1182(3)	?	
cis	A_1(Ra.)	822(0)	516(5)				
	B_1(Ra.)		527(2)	?	1154(4)	?	318(1)
	B_2(Ra.)			?	?	710(0)	
	A_2(Ra.)			?	?	?	85(1)

Kohlrausch and Wittek, loc. cit., give another assignment of the frequencies of the dihalogen ethanes. They agree with Wu (Pp. 307-310) in that the Raman and the infrared data indicate the presence of both the trans and the cis forms, but differ from Wu in the assignment of certain frequencies. While such controversies probably have not much significance especially in view of the unsettled question concerning the structure of the isomers (see below), it may be well to point out some difficulties in their assignment of the frequencies. Thus for the trans form, they interchange the A vibrations at ~1050 cm^{-1} with the B' vibrations at ~1440 cm^{-1} in Table LXXXIV. Now the

Raman lines at ~1440 cm^{-1} are all depolarized, while as A vibrations they should have been polarized. On the other hand, the 1050 cm^{-1} of $C_2H_4Cl_2$ is polarized, while as a b' vibration according to them, it should have been depolarized.

For the cis form, they assign the Raman frequencies at ~1180 cm^{-1} (A_2 δ' in Table XC) to the A_1 class, and the $C_2H_4Br_2$ 1238, C_2H_4BrCl 1256p, $C_2H_4Cl_2$ 1263d, C_2H_4ClI 1231 to the B_1 class. Here the difficulties are: i) the $C_2H_4Cl_2$ 1263d line must be ascribed to the trans $C_2H_4Cl_2$ since it is shown by Mizushima and Morino not to disappear in the solid state, ii) the corresponding infrared bands have not been observed while as B vibrations according to these authors they should appear in absorption, and iii) the $C_2H_4Br_2$ 1186d and $C_2H_4Cl_2$ 1207d are depolarized, while as A_1 vibrations, they should have been polarized.

Instead of postulating the trans and the cis forms, Edgell and Glockler, Jour. Chem. Phys. 9, 375, (1941), suggest that the stable isomers are the trans form and a staggered form of symmetry C_2 which results when one CH_2X group is rotated about the C - C axis through 120° from the trans configuration. The arguments for the C_2 form are: i) the Cl - Cl distances for the trans and the C_2 forms are 4.4 and 3.1 A, respectively, in agreement with the values 4.4 ± 0.1 and 3.2 ± 0.1 given by Wierl from electron diffraction measurements, and ii) the number of depolarized Raman lines below ~1600 cm^{-1} expected from the trans, cis and C_2 form is 2, 9, 6 respectively. The number observed is 9 for $C_2H_4Cl_2$ and $C_2H_4Br_2$ according to the list of Kohlrausch and Wittek, loc. cit., while 11 would be expected for the trans + cis mixture.

While the electron diffraction data, if accurate, seem to demand the C_2 instead of the cis form, we wish to point out that the second argument above furnishes no evidence either way. The absence of certain expected Raman lines can always be due to low intensities. Consider, for example, the number of polarized Raman lines which in general should be more intense than the depolarized ones and are hence less likely to escape observation. The number below ~1600 cm^{-1} expected of the three isomers is 5, 5, 8 as shown in the following table.

	No. dep. lines below 1600 cm^{-1}		No. pol. lines below 1600 cm^{-1}	
	expected	observed	expected	observed
trans	2		5	
cis	9	9	5	8, $C_2H_4Cl_2$
C_2	6		8	7, $C_2H_4Br_2$

Thus for a trans +C_2 mixture, 13 polarized Raman lines would be expected compared with the 7 or 8 observed, whereas 10 are expected for the trans + cis mixture.

Another point may also be mentioned in this connection. There seems to be general agreement that the depolarized lines 92 cm^{-1} in $C_2H_4Br_2$ and 123 cm^{-1} in $C_2H_4Cl_2$ are the torsional frequency of the two CH_2X groups (Table XC and Kohlrausch and Wittek, loc. cit.). For the C_2 form, this mode of vibration is symmetrical with respect to the axis of symmetry and would give rise to a polarized line. For this and other reasons, an attempt to assign the observed Raman and infrared frequencies on the assumption of a trans +C_2 mixture has not been successful.

Symm. Tetrahalogen ethanes (V, §6, B, P. 312)

The Raman spectra of symm. $C_2H_2Cl_4$ and $C_2D_2Cl_4$ have been studied at two temperatures by Langseth and Bernstein, Jour. Chem. Phys. 8, 410, (1940). From a consideration of the number of lines below ~400 cm^{-1} having positive and negative temperature coefficients of intensity, these authors conclude that the isomeric forms of these molecules are the cis and the C_2 staggered forms, with the cis more stable.

It is found, however, by electron diffraction measurements by Shoemaker and Stevenson, Jour. Chem. Phys. 8, 637, (1940), that the Cl - Cl distances in $C_2H_2Cl_4$ are 3.31 and 4.32A corresponding to the distances 3.25 and 4.32A expected of the C_2 staggered and the trans form respectively.

From the Raman spectrum data now available, it does not seem possible to give a complete and satisfactory analysis of the observed frequencies and hence to decide the isomeric forms of the molecules. In view of the electron diffraction data, Langseth and Bernstein's conclusion must be regarded as premature.

CH_3CF_3, CH_3CCl_3 (V, §6, B, P. 312)

The Raman spectrum of CH_3CF_3 has been studied by Hatcher and Yost, Jour. Chem. Phys. 5, 992, (1937); and that of CH_3CCl_3 by Hull, ibid., 3, 534, (1935). Irrespective of whether it is the staggered or the eclipsed structure which is the more stable one, the symmetry class is C_{3v}. There should be 5 || vibrations giving polarized Raman lines, 6 ⊥ and doubly degenerate vibrations giving depolarized lines, and a torsional vibration inactive in Raman effect.

In the absence of polarization data, the following tentative assignment of the observed frequencies can be made:

	A(||)					E(⊥)						A'
	$\nu(CH_3)$	$\delta(CH_3)$	$\nu(CC)$	$\nu(CX_3)$	$\delta(CX_3)$	$\nu(CH_3)$	$\delta(CH_3)$	$\nu(CX_3)$	$\delta(CX_3)$	δ'	δ''	torsion
CH_3CF_3	2947	1450	829	968	603	3040	?	1279	358	?	541	?
	(5)	(4)	(5)	(6)	(2)	(4)		(1)	(2)		(2)	
CH_3CCl_3	2943	1424	714	523	345	3010	1361	1071	241	?	?	?
	(9)	(2)	(7)	(9)	(10)	(6)	(2)	(2)	(7)			

CH_3CF_3: 2792(2) = 1450 + E(1350), 2825(1) = ?, 1885(1) = 2 1450

CH_3CCl_3: 1242($\frac{1}{2}$) = 523 + 714, 1592($\frac{1}{2}$) = 523 + 1071, 2743($\frac{1}{2}$) = 1424 + 1361.

The Raman spectra of a number of halogen ethanes have been studied.

$CHCl_2CH_2Cl$ by Hull, loc. cit.;
$CFCl_2CFCl_2$ by Glockler and Sage, Jour. Chem. Phys. 8, 291, (1940);
CF_3CCl_3, CCl_3CHFCl, CF_2ClCF_2Cl, $CF_2ClCFCl_2$, CF_2ClCF_2H, $CF_2ClCHFCl$, CF_2BrCF_2Br, $CF_2BrCFClBr$, by Glockler and Sage, ibid. 9, 387, (1941).

A discussion, at best tentative and uncertain, of these spectra will not be attempted here.

C_3H_6 cyclopropane (V, §7, P. 313)

A complete normal coordinate treatment of this molecule has been given by Saksena, Proc. Ind. Acad. Sc. A 10, 449, (1939). The potential employed is of the modified valence force type:

$$2V = k_{CC}\Sigma(\Delta R)^2 + k_{CH}\Sigma(\Delta r)^2 + k_{CCC}\Sigma(a\Delta\psi)^2 + k_{HCH}\Sigma(b\Delta\varphi)^2$$
$$+ k_{CCH}\Sigma(b\Delta\gamma)^2 + k_8\Sigma(\Delta R)(b\Delta\varphi) + k_7\Sigma(\Delta R)(\Delta r).$$

From the two A_2'' vibrations (see Table XCII), Saksena finds

$$k_{CH} = 4.9 \times 10^5, \qquad k_{CCH} = 0.45 \times 10^5.$$

With these values and the $3A_1'$ vibrations, he finds

$$k_{CC} = 4.06 \times 10^5, \quad k_{HCH} = 0.348 \times 10^5, \quad k_8 = -0.547 \times 10^5, \quad k_7 = -0.153 \times 10^5.$$

The constant k_{CCC} is taken to be -0.923×10^5 for the calculation of the 4 E' vibrations. The low value k_{CC} for the C – C bond is to be noted. It is not clear, however, from the paper how it is possible to obtain any unique values for the 4 constants k_{CC}, k_{HCH}, k_8, k_7 from only 3 equations for the 3 A_1' vibrations.

$(CH_3)_2O$ dimethyl ether (V, §2, P. 315)

The infrared spectrum has been studied under low dispersion by Crawford and Joyce, Jour. Chem. Phys. 7, 307, (1939), who also summarizes the Raman spectrum data obtained by Dadieu and Kohlrausch, Monats. f. Chem. 57, 225, (1931); Kohlrausch, ibid. 68, 349, (1936); Sirkar, Ind. J. Phys. 7, 257, (1932); Volkenstein and Syrkin, Nature 137, 288, (1937); Ananthakrishnan, Proc. Ind. Acad. Sc. A 5, 285, (1937).

On the assumption of a model with symmetry $C_{2\upsilon}$, the observed infrared and Raman frequencies can be assigned as follows:

	Symmetry (σ, υ)						
Nature of vibration	A_1(s, a)		B_1(s, a)		B_2(a, s)		A_2(a, a)
	Infra.	Ra.	Infra.	Ra.	Infra.	Ra.	Ra.
$\nu(CH_3)$	(2915)	2810p	(2915)	?	(2915)	?	?
$\nu'(CH_3)$	(2915)	2911p	-	-	(2915)	?	-
$\delta_\perp(CH_3)$	(1466)	?	(1466)	(1450d)	(1466)	(1450d)	(1450d)
$\delta_\parallel(CH_3)$	(1466)	?	-	-	?	?	-
$\tau_M(CH_3$ rocking)	(1180)	?	(1180)	(1155d)	(1180)	(1155d)	(1155d)
$\nu(CO)$	(940)	920p	-	-	1122	1110?	-
δ_M(C-9-C)	440	412p	-	-	-	-	-
γ(torsion)	-	-	?	?	-	-	?

σ = plane bisecting the C – O – C angle; υ = plane of C – O – C. s, a = symmetric and antisymmetric with respect to σ or υ. Frequencies in parentheses indicate frequencies falling together and unresolved.

The potential barrier for the internal rotation of the CH_3 groups has been calculated by Kistiakowsky and Rice from entropy data to be ~2500 cal/mol. (~870 cm^{-1}). Jour. Chem. Phys. 8, 618, (1940). It is possible that the very weak Raman line at ~300 cm^{-1} arises from the torsional vibrations.

$(CH_3)_2S$ dimethyl sulfide (V, §7, 2, P. 315)

The Raman spectrum and the infrared spectrum under low dispersion have been studied by Fonteyne, Jour. Chem. Phys. 8, 60, (1940), and the latter has again been studied by Thompson, Trans. Faraday Soc. 37, 38, (1941). The observed frequencies and their assignments on the basis of a $C_{2\upsilon}$ model are given below. The notations are the same as for $(CH_3)_2O$.

Nature of vibration	Symmetry (σ, υ)						
	$A_1(s,s)$		$B_1(s,a)$		$B_2(a,s)$		$A_2(a,a)$
	Infra.	Ra.	Infra.	Ra.	Infra.	Ra.	Ra.
$\nu_{\parallel}(CH_3)$	(2924)	2832p	(2924)	2852	(2924)	?	2980d
$\nu_{\perp}(CH_3)$	(2924)	2911p	-	-	?	?	-
$\delta_{\perp}(CH_3)$	(1430)	(1440)	(1460)	(1440)	(1430)	(1440)	1420d
$\tau_{\parallel}(CH_3)$	(1315)	1325p	-	-	(1315)		-
$\delta_M(CH_3$ rocking$)$	1242	1230	1274	?	1040	1041vw	919vw
$\upsilon(CS)$	693	690p	-	-	?	742d	-
$\delta_M(C-S-C)$	?	285p	-	-	-	-	-
γ(torsion)	-	-	?	?	-	-	?

Electron diffraction measurements by Brockway and Jenkins, J. Am. Chem. Soc. 58, 2036, (1936), give 1.82A for the C-S distance. The angle $\widehat{CSC}$ is less certain, but is probably $\sim 105^{0}$.

The potential barrier for the internal rotation of the CH_3 groups has been calculated from the measured entropy and on the basis of the above fundamentals by Osborne, Doescher and Yost, Jour. Chem. Phys. 8, 506, (1940), and by Thompson, loc. cit. The value is ~2000 cal/mol.

$(CH_3)_2Zn$ dimethyl Zinc (V, §7, 3, P. 315)

The Raman spectrum has been studied by Venkateswaran, Ind. J. Phys. 5, 145, (1930), and Pai, Proc. Roy. Soc. A149, 29, (1935). The infrared spectrum has been studied by Thompson, Linnett and Wagstaffe, Trans. Faraday Soc. 36, 797, (1940). Measurements of the electric moment (Braune and Knoke, Zeits. f. phys. Chem. B 23, 410, (1933))seem to indicate a linear C-Zn-C structure. The molecule would then be similar to dimethyl acetylene in the normal vibrations and their selection rules. Thompson et al from considerations of the assignments of the infrared bands on the basis of the eclipsed D_{3h} and the staggered D_{3d} models that the former is more satisfactory. The appearance of the frequency 620 cm^{-1}, which is probably the "rocking" frequency of the CH_3 groups, in both the Raman and the infrared spectrum seems to prefer D_{3h} over D_{3d}. It is probable that on account of the greater distance apart (than in C_2H_6) between the two C atoms the potential barrier for the torsion oscillation is rather low, perhaps <1000 cal/mol., so that the symmetry is D'_{3h} (see P. 296). In the following table, the observed data are summarized together with their assignments on the basis of the D_{3h} model.

The assignments suggested here differ from those given by Thompson et al chiefly in the deformation vibrations of the CH_3. The reason for assigning the infrared frequency 1350 cm^{-1} and the Raman line 1346 cm^{-1} to the parallel vibrations $\delta_{\parallel}(CH_3)$ in A_1' and A_1'' and the infrared and Raman frequency at 1445 cm^{-1} to the $\perp$ vibrations $\delta_{\perp}(CH_3)$ in E' and E" is that the corresponding vibrations in C_2H_6 and CH_3CCCH_3 have these values. Reference to the foregoing tables for $(CH_3)_2O$ and $(CH_3)_2S$ shows that the $\parallel$ and $\perp$ deformation vibrations in CH_3 have frequencies ~1310 and ~1440 respectively. The assignment of the Raman line 1160 to the rocking vibration of CH_3 in E" is suggested by the corresponding vibration in C_2H_6 (see Table LXXXV, P. 304), although the intensity seems too great.

			Here suggested Infra.	Ra.	Thompson et al Infra.	Ra.	Obs. ν	*Assignment*
A_1'	ν_1	$\nu_{\parallel}(CH_3)$	-	2890s	-	2890s	248Ra	$2\nu_4$
	ν_2	$\delta_{\parallel}(CH_3)$	-	1346w	-	1160s	488Ra	$\nu_{10} - \nu_4$
	ν_3	$\nu_{\parallel}(CZn)$	-	505s	-	505s		
A_2''	ν_5	$\nu_{\parallel}(CH_3)$	(2924)	-	(2924)	-	1180s	$\nu_3 + \nu_7$
							1305w	$\nu_{11} + \nu_{14}$
	ν_6	$\delta_{\parallel}(CH_3)$	1350w	-	1180s	-	1541vw	$\nu_{11} + \nu_{13}$
	ν_7	$\nu_{\parallel}(CZn)$	704s	-	704	-	1692m	$2\nu_3 + \nu_7$
A_1''	ν_4	torsion	- (130)		-(130)-		1789w	$\nu_{10} + \nu_{14}$
E'	ν_8	$\nu_{\perp}(CH_3)$	(3000)	?	(3000)	?	1887vw	$\nu_3 + \nu_9$; $\nu_3 + \nu_8$
							2105vw	$3\nu_7$
	ν_9	$\delta_{\perp}(CH_3)$	1445w	1443?	1350m	1346w	3450s	$\nu_3 + \nu_5$; $\nu_3 + \nu_8$
	ν_{10}	δCH_3 rocking	617s	620m	617s	620m	4167w	$\nu_8 + \nu_{14}$
	ν_{11}	$\delta(C-Zn-C)$	?	144w	?	144w	4386m	$\nu_8+\nu_9$; $\nu_8+\nu_{13}$; $\nu_9+\nu_{12}$
							5781w	$\nu_1+\nu_5$; $\nu_1+\nu_8$, *etc.*
E''	ν_{12}	$\nu_{\perp}(CH_3)$	-	(3000)	-	(3000)		
	ν_{13}	$\delta_{\perp}(CH_3)$	-	(1440)	-	?		
	ν_{14}	δCH rocking	-	1160s	-	?		

On the basis of the fundamentals suggested here, all the observed infrared bands between 9 and 2μ can be accounted for (for selection rules for harmonic and combination bands, see Pp. 296-7). The value ~130 cm^{-1} for the torsional oscillation is assumed to explain the weak Raman line 248 cm^{-1}.

POTENTIAL CONSTANTS OF POLYATOMIC MOLECULES

In recent years, the detailed calculation of the potential functions of polyatomic molecules has been the subject of study by a number of investigators. Before summarizing in the table at the end of this section the best molecular constants now available, it is perhaps not entirely out of place to emphasize again the factors affecting the potential constants and the extent to which significance may be attached to their exact numerical values.

1) Form of the potential function

It has been sufficiently recognized that while the bond constants in potentials of the modified valence force type, for example, do have simple physical meaning, their exact numerical values depend on the form of the potentials in which they are defined, i.e., on whether certain cross terms are included. As an example, consider the methyl halides. A simple valence potential contains 4 constants, while better approximations are obtained by introducing additional cross terms. Thus

$$2V_A = k\,\Sigma(\delta r)^2 + k_1(\delta r_0)^2 + k_\theta\Sigma(r\delta\theta)^2 + k_\varphi\Sigma(r\delta\varphi)^2 \qquad (A)$$

$$2V_B = 2V_A + 2k_4\delta r_0\Sigma(r\delta\varphi) \qquad (B)$$

$$2V_C = 2V_B + 2k_5\Sigma(r\delta\theta)(r\delta\varphi) \qquad (C)$$

where r and r_0 are the C-H and C-X distances respectively, θ is the $\widehat{HCH}$ angle, and φ the $\widehat{HCX}$ angle. In the following table, the values under column A are obtained from the parallel vibrations for the potential (A), (P. 242). Those under B are obtained by Linnett, Jour. Chem. Phys. 8, 91, (1940), by fitting the 5 constants in (B) to the observed frequencies ν_2, ν_3, ν_4, ν_5, ν_6. Those under C are obtained by Crawford and Brinkley, ibid. 9, 69, (1941), by taking over the values of k and k_θ in (C) from C_2H_6 and determining the other 4 constants such that the calculated frequencies from the determinantal equation best fit the observed values (the maximum discrepancy between the calculated and the observed frequencies is 1.7% in this case).

	A			B				C			
	k(C-H)	k_1(C-X)	$k_\theta+k_\varphi$	k(C-H)	k_1(C-X)	k_θ	k_φ	k(C-H)	k_1(C-X)	k_θ	k_φ
CH_3F	4.96	5.78	0.98	4.71	5.64	0.433	0.792	4.79	5.96	0.46	0.76
CH_3C	4.94	3.46	0.97	4.90	3.35	0.438	0.587	4.79	3.64	0.46	0.58
CH_3Br	4.94	2.82	0.82	4.95	2.83	0.432	0.529	4.79	3.13	0.46	0.52
CH_3I	4.96	2.23	0.77	5.00	2.32	0.432	0.460	4.79	2.65	0.46	0.45

Of the 3 sets of potential constants, those under A may be regarded as definitely inferior since they have been obtained without making use of the perpendicular vibrations. Both sets B and C reproduce the observed frequencies about equally well. It is seen that even for the same molecule CH_3I, the constant k differs by about 4% and k_1(C-I) by about 12% in the two calculations. Hence it is abundantly clear that great care must be exercised in comparing the bond constants in different molecules which are structurally different and consequently for which the potentials employed cannot be exactly comparable.

2) Method of the calculation

The above two sets of constants B and C also illustrate the difference in the constants resulting from a difference in the procedure adopted in their evaluation. The procedure of Crawford and Brinkley in which the constants pertaining to certain groups or radicals are carried over from other molecules is useful for i) determining a potential function with a large number of constants and hence giving a better description of the molecule, and ii) locating a priori the fundamental frequencies of a new molecule. Thus Crawford, Jour. Chem. Phys. 8, 526, (1940), employs for CH_3CCH a potential function with 13 constants 5 of which are carried over from C_2H_6, 4 from C_2H_2, and 3 from dimethyl acetylene.

On the other hand, the usual procedure of determining the potential constants for each individual molecule independently of others has the advantage that the potential so determined is characteristic of that molecule. Thus the k(C-H) constants under B in the above table show a small increase in passing from CH_3F to CH_3I. This increase, if shown to be free of the effect of anharmonicity discussed below, would mean a slight decrease in the C-H distance in passing from CH_3F to CH_3I. As matter stands, however, there is no exact criterion for choosing either one of the two sets B and C, since both reproduce the observed frequencies about equally well. Perhaps a choice in this and similar cases will remain to be decided by the particular object of the calculation and by individual preference. In any case, it is useful to remember the limitations of the calculation and the inherent indefiniteness of the constants within certain range.

3) Anharmonicity

Now the determinantal equation of a normal coordinate treatment gives the so-called zeroth-order frequencies ω's, while the observed frequencies are determined not only by the quadratic potentials alone, but also by the effect of anharmonicity. For vibrations involving H atoms, it is found from the few cases for which a higher order calculation has been made (H_2O, C_2H_2, HCN, CH_4) that the potential constants obtained with the ω's may differ from those calculated with the observed ν's by as much as 10% (see footnotes on Pp. 156, 163, 184). For vibrations not involving H atoms, the difference is in general small, but in some cases it may still be 4-6% (for COS, the constants obtained with the ω's and the ν's are, respectively, k(CO) = 13.4, k(CS) = 8.35; k(CO) = 14.2, k(CS) = 8.0, in 10^5 dynes/cm. See P. 151). Since the evaluation of the ω's cannot be carried out in most cases for lack of appropriate data, one must be contented with an approximate determination of the potential functions from the observed frequencies.

One might suppose that if one calculates the potential functions consistently from the observed ν's in all cases, the anharmonicity may affect the potential constants by approximately the same amount in different molecules so that the potential constants are still relatively correct. This is undoubtedly true. But when one insists on attaching a significance to small variations of the order 1-2%, in the bond constants in a series of molecules, it may be well to keep in mind the fact that the effect of anharmonicity on the frequencies depends in general on the motion of all the atoms in the molecule, and consequently the frequencies of even an identical group (i.e., group having identical potential functions) in different molecules may be differently affected. The result is that the observed ν's will lead to slightly different potential constants for the group in different molecules, although the ω's, if available, would lead to identical constants.

4) Numerical uncertainties

Quite often it happens that simply because of the nature of the determinantal equation, the values of certain potential constants are exceedingly sensitive to small changes in the frequencies. In unfavorable cases, such as C_2H_4 discussed in an earlier section, it is found that a change of the frequencies by 1% may spell the difference between real and complex roots for certain constants (k_3 in the case of C_2H_4). As the corrections for anharmonicity are not known in general, one should perhaps regard the potential constants as significant only up to a few per cent in such cases.

Finally, in view of the still frequent over-simplification in the literature, it may not be entirely superfluous to emphasize that one should not dwell too much in the "characteristic frequencies" themselves of certain chemical bonds or groups. It is really the bond constant, not the frequency, that is characteristic of a bond. In a complex molecule, a "characteristic bond frequency" is not determined by the potential constant and the masses of the atoms of that bond alone, but is a normal frequency of the molecule as a whole. A shift of the characteristic frequency in passing from one to another molecule does not necessarily mean a corresponding change in the bond constant. For example, the shift of the C≡C frequency at 1960 cm^{-1} in C_2H_2 to 2130 cm^{-1} in CH_3CCH and 2270 cm^{-1} in CH_3CCCH_3 is taken by Hibben (The Raman Effect and Its Chemical Applications, P. 201) to mean an increase in the C≡C bond constant in the substituted acetylenes. Calculations (Pp. 292, 318; also Crawford, Jour. Chem. Phys. 7, 555, (1939); 8, 526, (1940)) on a normal coordinate treatment show, however, that these observed frequencies are entirely consistent with one value for the C≡C constant in these molecules. The increase in the C≡C frequencies in the substituted acetylenes is due to the coupling of the motions of the various atoms and not to an increase in the bond constant. For this reason, any discussion of the bond or group structure must be based on the bond constants calculated from an appropriately defined potential function, but not on the frequencies which can be "characteristic" of a bond or group only in a qualitative sense.

	$-CH_3$	$=CH_2$	$\equiv CH$	C–C	$C \overset{\cdots}{=} C$	C=C	C≡C	Ref.
CH_4	*5.835(1.093)							D;S
	5.7							225
CH_3F	4.71							L
CH_3Cl	4.91							L
CH_3Br	4.95							L
CH_3I	5.00							L
CH_3OH	4.80 (1.108)							285
CH_3CN	5.0			5.3				L
	4.79			4.94(1.49)*				C_3
CH_3NC	5.0							L
CH_3CCH	4.79		5.85	5.18(1.462)			15.58	C_2
CH_3CCCH_3	4.79			5.18			15.59	C_1
C_2H_6	4.81			4.53(1.54)*				L
C_2H_4		5.02(1.071)				9.9(1.353)		S
OCH_2		4.2						211
$OCCH_2$		4.85				9.8(1.35)*		253
$C(CH_2)_2$		4.9				9.5(1.31)*		290
C_3H_6		4.85		5.17				315
		4.9		4.06(1.53)				Se;S
C_6H_6		5.05			7.58(1.39)*			321
C_2N_2					6.7 (1.37)*			187
C_2Cl_4					6.8 (1.38)*			272
HCN			*6.3					156
			5.85(1.06)					C_3
C_2H_2			*6.2				*17.0	185
			5.85(1.057)				15.59(1.204)	C_1
C_4H_2			5.95		3.6 (1.36)*		16.3 (1.187)*	259
C_3O_2							12.5 (1.29)*	216

Table CI,a. Potential constants in 10^5 dynes/cm. and bond distances in 10^{-8} cm.

Potential constants marked with * are calculated from the zeroth-order ω's; those unmarked from the observed frequencies. Numbers in parentheses are distances. Those marked with * are electron diffraction values; those unmarked from the spectra. D = Dennison. Rev. Mod. Phys. 12, 175. (1940); L = Linnett, Jour. Chem. Phys. 8, 91, (1940); C_1 = Crawford, ibid. 7, 555, (1939); C_2 = Crawford, ibid. 8, 526, (1940); C_3 = Crawford and Brinkley, ibid. 9, 69, (1941); Se = Seksena, Proc. Ind. Acad. Sc. A10, 449, (1939); S = this Supplement; numbers refer to page numbers in this volume.

	C - O	C = O	$C \mathrel{\underset{\cdots}{=}} O$	$C \equiv N$	Ref.
CH_3OH	5.77(1.427)				285
OCN^-	4.69			16.57	158
$CO_3^=$	6.2				208
$OCCl_2$		12.1(1.28)*			213
OCH_2		12.1(1.21)			211; S
$OCCH_2$		12.3(1.17)*			253
OCS		*13.4(1.16)*			151
		14.2			151
CO_2			15.9(1.15)		147
C_3O_2		16.0(1.20)			216
SCN				14.4	158
SeCN				14.6	158
HCN				*16.2(1.15)	156
				17.7	C_3
C_2N_2				17.5(1.155)*	187
CH_3CN				17.5(1.16)*	L; C_3
CH_3NC				16.3(1.17)*	L
XCN, X= halogen				16.7(1.17)*	157

Table CI,b. Potential constants in 10^5 dynes/cm. and bond distances in 10^{-8} cm.

	C - F	C - Cl	$C - B_X$	C - I	
$OCCl_2$		2.27(1.68)*			213
XCN		5.2 (1.67)*	4.2 (1.79)	2.9 (1.96)	157
C_2Cl_4		4.5 (1.73)*			272
$C_2H_2Cl_2$,	trans	4.0 (1.69)*			275
CH_3X	5.64(1.42)*	3.35(1.77)*	2.83(1.91)*	2.32(2.28)*	L
	5.96(1.39)	3.64(1.66)	3.13(1.88)	2.65(2.07)	C_3
CX_4	5.4 (1.36)*	1.7 (1.76)*	1.4 (1.93)*	(2.14)*	233

Table CI,c. Potential constants in 10^5 dynes/cm. and bond distances in 10^{-8} cm.